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**NUCLEAR SCIENCE SERIES**

**The Radiochemistry  
of Germanium**

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# The Radiochemistry of Germanium

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Subcommittee on Radiochemistry  
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## FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman  
Subcommittee on Radiochemistry

## INTRODUCTION

This volume which deals with the radiochemistry of germanium is one of a series of monographs on the radiochemistry of the elements. A review of the nuclear and chemical features of particular interest to the radiochemist is presented together with a discussion of sample dissolution and activity measurement techniques. A collection of radiochemical procedures for the element as found in the literature is also included.

The information that is presented herein was obtained from the general review references that are cited and from a search of the Chemical Abstracts from 1941 to June 1961 and the Nuclear Science Abstracts from 1948 to June 1961. Plans include revision of the monograph periodically when new techniques and procedures warrant its modification. The reader is encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of germanium which might be included in a revised version of the monograph.

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## The Radiochemistry of Germanium

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### I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF GERMANIUM

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## II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF GERMANIUM

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## III. ISOTOPES OF GERMANIUM

TABLE 1. ISOTOPES OF GERMANIUM \*

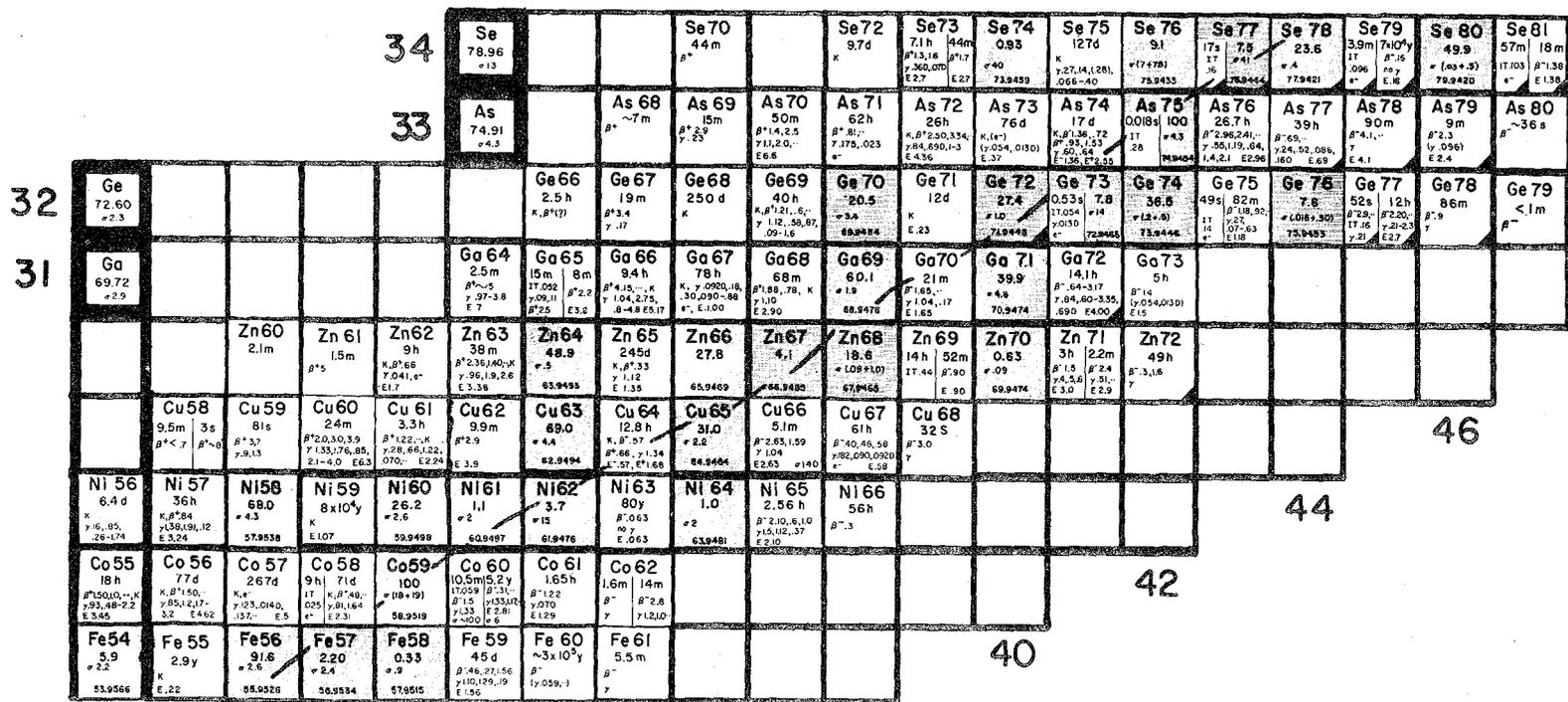
Isotope	Half-life	Method of Preparation	Types of Decay	Energy of Radiations in Mev.
$^{65}_{32}\text{Ge}$	1.5 m	$\text{Zn}^{64}(\alpha, 3n)\text{Ge}^{65}$	$\beta^+$ $\gamma$	3.7 0.67, 1.72
$\text{Ge}^{66}$	150 m	$\text{As}^{75}(\text{d}, \alpha 7n)\text{Ge}^{66}$ $\text{Zn}^{64}(\alpha, 2n)\text{Ge}^{66}$	$\beta^+(?)$ $\gamma$	0.045(100%); 0.070(20%); 0.114(50%); 0.186 scint spect.
$\text{Ge}^{67}$	21 m	$\text{As}^{75}(\text{d}, \alpha 6n)\text{Ge}^{67}$	$\beta^+$ $\gamma$	2.9 0.17, 0.68, 0.86, 1.47
$\text{Ge}^{68}$	280 d	$\text{As}^{75}(\text{d}, \alpha 5n)\text{Ge}^{68}$ $\text{Zn}^{66}(\alpha, 2n)\text{Ge}^{68}$	EC $\gamma$	none
$\text{Ge}^{69}$	40.4 h	$\text{Ge}^{70}(\text{n}, 2n)\text{Ge}^{69}$ daughter $\text{As}^{69}$ $\text{Ga}^{69}(\text{d}, 2n)\text{Ge}^{69}$ $\text{Zn}^{66}(\alpha, n)\text{Ge}^{69}$	EC (67%) $\beta^+$ (33%) $\gamma$	1.215(88%); 0.610(10%); 0.22(2%) 0.090, 0.388, 0.576, 0.870, 1.12, 1.34, 1.61
$\text{Ge}^{70}$	Stable (20.55%)			
$\text{Ge}^{71}$	11.4 d	$\text{Ge}^{70}(\text{n}, \text{p})\text{Ge}^{71}$ daughter $\text{As}^{71}$ $\text{As}^{75}(\text{d}, \alpha 2n)\text{Ge}^{71}$ $\text{Ga}^{71}(\text{d}, 2n)\text{Ge}^{71}$ $\text{Ge}^{70}(\text{d}, \text{p})\text{Ge}^{71}$	EC $\gamma$	none
$\text{Ge}^{72}$	Stable (27.37%)			
$\text{Ge}^{73\text{m}}$	0.53 s	$\text{Ge}^{72}(\text{n}, \text{r})\text{Ge}^{73\text{m}}$ daughter $\text{As}^{73}$	IT	0.0135, 0.0539

TABLE 1. (Continued)

Isotope	Half-life	Method of Preparation	Types of Decay	Energy of Radiations in Mev.
Ge <sup>73</sup>	Stable (7.67%)			
Ge <sup>74</sup>	Stable (36.74%)			
Ge <sup>75m</sup>	48 s	Ge <sup>74</sup> (n,γ)Ge <sup>75m</sup> Ge <sup>76</sup> (n,2n)Ge <sup>75</sup> Ge <sup>74</sup> (d,p)Ge <sup>75m</sup> U <sup>235</sup> (n,f)	IT	0.139
Ge <sup>75</sup>	82 m	Ge <sup>74</sup> (n,γ)Ge <sup>75</sup> Ge <sup>76</sup> (n,2n)Ge <sup>75</sup> As <sup>75</sup> (n,p)Ge <sup>75</sup> Se <sup>78</sup> (n,α)Ge <sup>75</sup> U <sup>235</sup> (n,f)	β <sup>-</sup> γ	1.14(85%), 0.614(15%) 0.066(2.2%); 0.199(12%); 0.264(100%); 0.427(2.5%); 0.477(2.3%); 0.628(1.8%)
Ge <sup>76</sup>	2x10 <sup>16</sup> y (7.67%)			
Ge <sup>77m</sup>	54 s	Ge <sup>76</sup> (n,γ)Ge <sup>77m</sup> Ge <sup>76</sup> (d,p)Ge <sup>77m</sup> U <sup>235</sup> (n,f)	β <sup>-</sup> (86%) IT (~14%) calc	2.7 0.159 (100% IT) 0.215(100% with β <sup>-</sup> )
Ge <sup>77</sup>	11.3 h	Ge <sup>76</sup> (n,γ)Ge <sup>77</sup> Ge <sup>76</sup> (d,p)Ge <sup>77</sup> U <sup>235</sup> (n,f)	β <sup>-</sup> γ	2.196(42%), 1.379(35%), 0.71(23%) complex spectrum
Ge <sup>78</sup>	86 m	U <sup>235</sup> (n,f)	β <sup>-</sup>	0.9 abs.
Ge <sup>79</sup>	<1 m		β <sup>-</sup>	

\* For more complete information on the radiations of the germanium isotopes and for references to the original literature consult: "Table of Isotopes," D. Strominger, J. M. Hollander and G. T. Seaborg, Reviews of Modern Physics, 30, No. 2, Part II, 640-642, (1958); Nuclear Data Sheets, National Academy of Sciences, National Research Council, C. L. McGinnis, editor.

FIGURE I. Chart of Germanium Nuclides



Reproduced from the G. E. Chart of the Nuclides (KAPL) 5th Edition,  
 Revised to April 1956; for more detail see Trilinear Chart of  
 Nuclides, W. H. Sullivan, Oak Ridge National Laboratory.

TABLE 2a. DECAY CHAINS AND YIELDS OF GERMANIUM  
NUCLIDES FROM THERMAL-NEUTRON FISSION OF U<sup>235\*</sup>

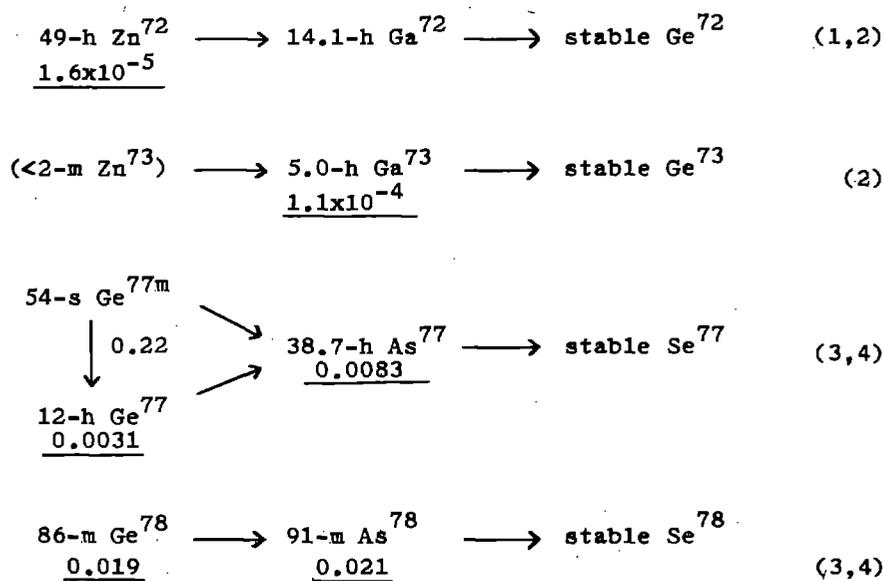


TABLE 2b. TOTAL CUMULATIVE YIELDS OF  
Ge<sup>77</sup> FROM U, Th AND Pu

	U <sup>233</sup> (thermal) (1,2)	Pu <sup>239</sup> (thermal)	Pu <sup>239</sup> (fast)	U <sup>235</sup> (14 Mev)	U <sup>238</sup> (fast)	Th <sup>232</sup> (fast) (5)	Th <sup>232</sup> (~8 Mev) (6)
12-h Ge <sup>77</sup>	0.010					0.009	0.022

\*Reproduced from Nucleonics Data Sheet No. 24, "Fission-Product Yields from U, Th, and Pu," authored by S. Katcoff, Nucleonics 16, No. 4, pp. 78-85, 1958.

#### IV. REVIEW OF CHEMISTRY OF GERMANIUM OF INTEREST TO RADIOCHEMISTS

##### 1. Metallic Germanium

Germanium is a relatively uncommon substance making up about 10<sup>-11</sup> percent of the earth's crust. It was discovered in the

mineral argyrodite,  $4\text{Ag}_2\text{S}\cdot\text{GeS}_2$ . Its chief occurrence is in certain zinc blendes and a major source of supply is by-product obtained in the smelting of zinc.

The element resembles carbon and silicon in having the  $ns^2np^2$  electron configuration and  $^3P$  ground state and in forming the tetrahedral bonds associated with  $sp^3$  hybridization. Elementary germanium possesses the diamond structure that characterizes carbon, silicon and gray tin. An amorphous form is also known. Germanium, like silicon, is a semiconductor. In the purest form it has a specific resistance at room temperature of about 50 ohm/cm the resistivity decreasing with rising temperature.

The metal is silvery-white, hard and brittle. It melts at  $959^\circ\text{C}$  and boils at  $2700^\circ\text{C}$ . Additional properties of the metal are:

Density (g/cc)	5.36
Atomic Volume	13.55
Ionization Potential (ev)	8.13
	(ev) 15.86
Atomic Radius ( $\text{A}^\circ$ )	1.22
Ionic Radius $M^{4+}$ ( $\text{A}^\circ$ )	0.53
Specific Heat (cal/g)	0.074
Hardness (Moh's Scale)	6.0-6.5

Germanium is only partially deposited by electrolysis of acid solutions. Electrolysis with a mercury cathode in dilute sulfuric acid solution, however, apparently quantitatively deposits germanium in the mercury cathode.<sup>(7)</sup> It deposits completely from alkaline solutions containing oxalate, tartrate, phosphate, carbonate or hydroxide ion as well. Careful control of conditions is required to obtain a bright adherent deposit. Electrodeposition of germanium from solutions of  $\text{GeI}_4$  in ethylene glycol<sup>(8)</sup> and  $\text{GeCl}_4$  in propylene glycol<sup>(9)</sup> produces a thick metallic film. Electrolysis of a solu-

tion of germanium (IV) oxide in fused borax<sup>(8)</sup> or potassium or sodium carbonate also deposits the metal.

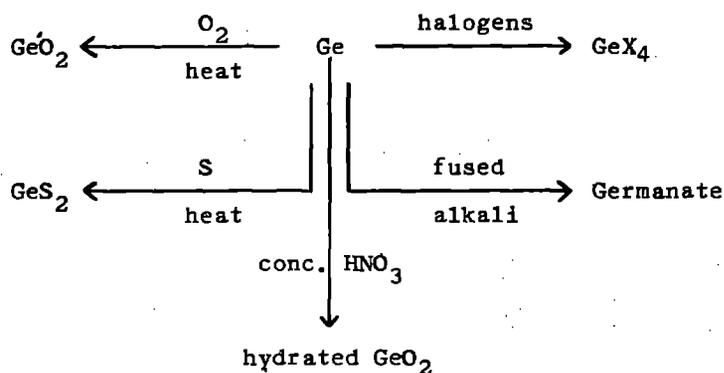
Germanium metal may also be prepared by reduction of germanium (IV) oxide by carbon or by mixed potassium cyanide and carbon under a molten sodium chloride flux. Germanium (II) oxide sublimes at 710°C and the layer of fused chloride prevents excessive losses of the element due to its volatility. Reduction with hydrogen can be carried out at temperatures as low as 500°C thereby removing the necessity for a protective fused salt blanket.

Very pure germanium is made by the method of zone refining.

Germanium metal is not appreciably affected by water, fifty percent sodium hydroxide, hydrochloric acid, sulfuric acid and hydrofluoric acid. It is tarnished by ten percent sodium hydroxide and concentrated nitric acid. Dilute nitric acid forms a germanium (IV) oxide film on the metal. The metal is dissolved by three percent hydrogen peroxide.

The principal reactions of germanium are as shown in Figure 2 below.

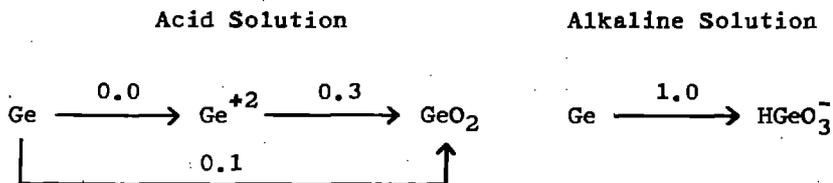
Figure 2. The Principal Reactions of Germanium



Germanium will displace silver from its solutions but will not displace copper,<sup>(10)</sup> mercury, tin, antimony or bismuth. Quanti-

tative oxidation state relationships are shown below in the potential diagram of Figure 3.

Figure 3. Potential Diagrams



## 2. Compounds of Germanium

Germanium, because of its position in the periodic table, is characterized by properties intermediate to those of silicon and tin below and above it. Germanium forms compounds in which the oxidation states are +2 and +4, the germanium (II) compounds being less common than those of germanium (IV). The +2 state is uncommon in silicon and is on the other hand more important in tin. This result is due to the fact that atomic size increases from silicon to tin thereby reducing the ability of the atoms to saturate themselves covalently. Tin, thus, is most likely to form an "inert pair" ion. The smaller tendency of germanium to form an "inert pair" ion results in a positive two state even more strongly reducing in character than divalent tin.

A brief discussion of the more important +2 and +4 compounds of germanium follows:

The hydrous monoxide of germanium is amphoteric. It is soluble in acids and alkalis, reactions with the latter yielding solutions of germanites. The solutions in hydrohalic acids in which the germanium is probably present in the form of halo complexes are rather stable in the absence of oxidizing agents. The germanium (II) on the other hand is converted to the germanate ion and hydrogen is evolved from highly alkaline solutions.

The germanium dihalides are not simple molecular compounds as are the tetrahalides but appear to be polymeric molecules in which the germanium atoms are bridged by halogens. They are unstable both toward hydrolysis and oxidation. Chloro and iodo complexes with the formulas  $MGeCl_3$  and  $MGeI_3$  have been prepared. These are easily hydrolyzed and are also readily oxidized by air.

The germanium (II) sulfide is the most stable germanium (II) compound known and may be melted and vaporized without decomposition. It is slightly soluble in water and hydrolyzes with the evolution of hydrogen sulfide. It dissolves in alkalis and in yellow ammonium sulfide.

Germanium dioxide is dimorphic, one modification possessing the quartz structure and the other the tetragonal rutile lattice, the latter form being stable below the transition temperature of  $1033^\circ\text{C}$ .

Solutions of germanium dioxide are slightly acidic. At pH values of 8.4 to 8.8 the principal ionic species is  $Ge_5O_{11}^{=}$  (rather than  $GeO_3^{=}$ ); the acid dissociation constant of  $H_2Ge_5O_{11}$  is about  $10^{-9}$ . At pH values above and below 8.4 to 8.8 lower stages of polymerization exist.

Germanium dioxide is amphoteric in nature. On treatment with concentrated hydrofluoric or hydrochloric acid conversion to the volatile tetrahalide occurs. Dissolution in solutions of alkali yields germanates; meta-,  $M_2GeO_3$  and ortho-germanates,  $M_4GeO_4$  have been reported.

The tetrahalides are volatile and their thermal stability decreases from the tetrafluoride to the tetraiodide. They are readily hydrolyzed. Germanium forms hexahalo complexes with fluorine and chlorine, the fluo complex  $GeF_6^{=}$  being rather

stable in water whereas the analogous chloro ion is rapidly hydrolyzed with the precipitation of the dioxide.

### 3. Separation of Germanium

Distillation of germanium tetrachloride is the standard way of separating germanium from other elements. It can be easily separated from elements such as arsenic, tin, antimony, selenium and tellurium halides by virtue of its lower boiling temperature. A stream of chlorine to keep the arsenic in the non-volatile quinquevalent state assures its complete removal from germanium.

The distillate obtained from a hydrobromic acid solution of a complex mixture such as fission products will, on the other hand, contain arsenic and selenium as well as traces of tin and antimony. The selenium present in the distillate can be removed by precipitation with hydroxylamine hydrochloride or with sulfur dioxide.

Also useful are the separations based on the use of hydrogen sulfide or alkaline sulfides. Germanium belongs with the elements of the arsenic group of sulfides and can be precipitated by hydrogen sulfide in acid solution and separated from the copper group by treatment of the sulfide with alkaline sulfide or polysulfide.

Germanium (IV) like tin (IV) forms a fluo anion in hydrofluoric acid solutions and can be separated from stannous tin, trivalent arsenic and antimony, lead and copper which precipitate with hydrogen sulfide.

A problem to the radiochemist is the incomplete precipitation and the almost colloidal form of the germanium(IV) sulfide<sup>(11)</sup> precipitate in acid solution. The precipitated sulfide also

tends to cause trouble with ordinary washing mediums and should be washed with six normal sulfuric acid that has been saturated with hydrogen sulfide.

Separation of germanium from arsenic, gallium, zinc, copper, iron, manganese, vanadium, titanium and zirconium but not molybdenum can be achieved by its precipitation with a freshly prepared five percent solution of tannin from chloride free solution about one tenth normal in sulfuric acid and three tenths molar in ammonium sulfate heated to about 95°C. Germanium is also precipitated quantitatively with tannin from oxalate solution at 0.07 N acidity.<sup>(12)</sup> The white precipitate that forms settles quickly, is easily filtered and washed. One precipitation provides separation from vanadium, zirconium, thorium, aluminum and iron (III). The acidity is below that required for tin and tantalum but above that needed for titanium.

Germanium (IV) compounds are reduced by sodium hypophosphite in acid solution to the soluble bivalent state while arsenic compounds are reduced to insoluble elementary arsenic which can then be removed by filtration.

The separation of germanium from zinc can also be achieved by selective reduction. In this case germanium is reduced to the metal form with zinc dust.

Monogermane can be reduced with hydrogen to deposit a germanium mirror similar to that obtained in the Marsh test for arsenic. This technique may be of potential importance to the radiochemist not only for separation purposes but also for sample preparation. The plating of germanium as a thin uniform film by this method could enhance the accurate measurement of weakly energetic beta emitting nuclides of germanium.

Germanium (IV) chloride is quite insoluble in concentrated

hydrochloric acid (0.3 mg per gram of acid at 0°C.) and can be separated from soluble chlorides such as arsenious, stannic and titanous by shaking with the acid in a separatory funnel. The chloride redissolves in fuming hydrochloric acid and is not reprecipitated from ether in the event solvent extraction is employed for the separation of other chlorides.

Aromatic organic reagents containing 2 phenol groups in ortho positions and a group that is ortho or para to one of them and capable of producing a prototropic system precipitate germanium. (13,14,15) For example, galloxyaniline, trihydroxyaurin, purpurogallin, 3,4 dihydroxyazobenzene and hematoxylin are specific precipitating reagents for germanium. The minimum germanium concentration that is needed for its precipitation as insoluble complex from a one percent solution of these particular reagents in a hydrochloric acid-ethanol mixture is listed below together with the color of the product precipitate.

TABLE 3. PRECIPITATION OF GERMANIUM

Reagent	Minimum Ge Conc. (grams/cc. solution)	Color of Precipitate
Galloyaniline	$2 \times 10^{-5}$	dark violet
trihydroxyaurin	$3 \times 10^{-7}$	violet
purpurogallin	$1 \times 10^{-5}$	rose
3,4 dihydroxyazobenzene	$4 \times 10^{-5}$	red
hematoxylin	$1.5 \times 10^{-6}$	red violet

Another precipitation method for germanium separation includes the addition of potassium ferrocyanide which forms a white precipitate tentatively assigned the formula  $(\text{GeO})_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ .

Germanium has been reported to be coprecipitated with silica during acid digestion of ore. (16) Coprecipitation of germanium on hydrated ferric oxide during the removal or excess hydrochloric acid in a volatilized germanium tetrachloride

sample has been employed in the preparation of germanium samples for colorimetric determination.<sup>(17)</sup> The applicability of these agents for preliminary separation steps in the radiochemical isolation of germanium is apparent.

Solvent extraction techniques are employed importantly in the separation and determination of germanium, the solvent extraction of germanium(IV) chloride for further treatment being standard operating procedure. In a typical determination the germanium, after quantitative removal as the tetrachloride from concentrated hydrochloric acid into benzene<sup>(18)</sup> or carbon tetrachloride<sup>(19)</sup> is back-extracted into water for additional purification.<sup>(20,21)</sup>

Separations based on the extraction of germanium (IV) halide into organic solvents are of special utility to the radiochemist. The difference in extraction behavior of Ge (IV) and As (III) in hydriodic acid-chloroform systems is, for example, the basis of a radiochemical separation of germanium and arsenic.<sup>(22)</sup> The large difference in the distribution of Ge (IV) and As (III) between concentrated hydrochloric acid solutions and the organic solvents, carbon tetrachloride, chloroform, bis (2-chloroethyl) ether and benzene has been employed for their separation also.<sup>(18)</sup>

Experimentally determined distribution ratios for Ge (IV) and As (III) as a function of hydrochloric acid concentration and organic solvent<sup>(23)</sup> are compared in Table 4 to show the large difference in the extraction behavior of Ge (IV) and As (III) at high hydrochloric acid concentration values.

The removal of impurities from germanium by selective extraction has received continuing attention. The separation of iron, antimony, tin, arsenic, selenium and germanium by extraction with methyl isobutyl ketone from hydrochloric acid solution has been investigated.<sup>(24)</sup> Tables 5 to 9 are presented to compare

the extraction behavior of various elements with germanium in several other systems. Germanium is not appreciably extracted whereas many of the elements are in most of the systems that are summarized in these tables. This type of information may be employed usefully by the radiochemist.

TABLE 4. DISTRIBUTION RATIO VERSUS HYDROCHLORIC ACID CONCENTRATION FOR As (III) AND Ge (IV) IN SEVERAL SOLUTIONS AT 30°C.

Hydrochloric (form wt/l)	Bis(2-chloro-ethyl) ether		Benzene		Chloroform		Carbon Tetra- chloride		Isopropyl ether	
	Ge	As	Ge	As	Ge	As	Ge	As	Ge	As
~ 2.1	0.020	0.012	0.0013	0.001	0.001	0.001	0.0006	0.0010	0.13	0.005
~ 4.2	0.034	0.017	0.026	0.006	0.023	0.01	0.015	0.003	1.3	0.078
~ 6.3	0.63	0.027	0.23	0.17	0.26	0.35	0.24	0.076	17.	0.75
~ 8.3	98.	2.9	64.	4.5	125.	3.3	125.	1.59	120.	1.32
~ 10.3	330.	12.5	292.	17.7	583.	6.9	597.	3.7	152.	0.30
~ 12.1	309.	13.0	434.	18.3	630.	7.3	594.	4.1	221.	----

TABLE 5. FLUORIDE EXTRACTIONS

Element	Oxidation State	Solvent System (before mixing)		Per Cent Extraction
		Aqueous Phase	Organic Phase	
Aluminum	Al(III)	20 M HF	Ethyl ether	0.2
Antimony	Sb(III)	3.5 M HF	Ethyl ether <sup>a</sup>	0.4
	Sb(III)	20 M HF	Ethyl ether	6.3
	Sb(V)	20 M HF	Ethyl ether	0.1
Arsenic	As(III)	4.6 M HF	Ethyl ether <sup>a</sup>	62
	As(III)	20 M HF	Ethyl ether	37.7
	As(V)	20 M HF	Ethyl ether	13.6
Beryllium	Be(II)	20 M HF	Ethyl ether	4.0
Cadmium	Cd(II)	20 M HF	Ethyl ether	1.4
Chromium	Cr(III)	20 M HF	Ethyl ether	<0.1
Cobalt	Co(II)	20 M HF	Ethyl ether	1.7
Copper	Cu(II)	20 M HF	Ethyl ether	1.3
Gallium	Ge(III)	20 M HF	Ethyl ether	<0.05
Germanium	Ge(IV)	20 M HF	Ethyl ether	6.7
Indium	In(III)	20 M HF	Ethyl ether	<0.05
Iron	Fe(II)	20 M HF	Ethyl ether	<0.1
	Fe(III)	20 M HF	Ethyl ether	<0.1
Manganese	Mn(II)	20 M HF	Ethyl ether	1.3
Mercury	Hg(II)	20 M HF	Ethyl ether	2.7

TABLE 5. (Continued)

Element	Oxidation State	Solvent System (before mixing)		Per Cent Extraction
		Aqueous Phase	Organic Phase	
Molybdenum	Mo(VI)	10 M HF, 6 M H <sub>2</sub> SO <sub>4</sub> , 2.2 M NH <sub>4</sub> F	Methyl isobutyl ketone <sup>b</sup>	9.7
	Mo(VI)	3.5 M HF	Ethyl ether <sup>a</sup>	9.1
	Mo(VI)	20 M HF	Ethyl ether	9.3
Nickel	Ni(II)	20 M HF	Ethyl ether	0.7
Niobium	Nb(V)	9 M HF, 6 M H <sub>2</sub> SO <sub>4</sub>	Diisopropyl ketone <sup>b</sup>	90
	Nb(V)	6 M HF, 6 M H <sub>2</sub> SO <sub>4</sub>	Diisobutylcarbinol <sup>b</sup>	98
	Nb(V)	10 M HF, 6 M H <sub>2</sub> SO <sub>4</sub> , 2.2 M NH <sub>4</sub> F	Methyl isobutyl ketone <sup>b</sup>	96
	Nb(V)	20 M HF	Ethyl ether	65.8
Phosphorus	P(V)	20 M HF	Ethyl ether	14.8
Protactinium	Pa(V)	8 M HCl, 0.6 M HF, sat. AlCl <sub>3</sub>	Diisopropyl ketone	~100
Rhenium	Re(VII)	20 M HF	Ethyl ether	61.8
Selenium	Se(IV)	4.6 M HF	Ethyl ether <sup>a</sup>	3.1
	Se(IV)	20 M HF	Ethyl ether	12.9
Silicon	Si(IV)	20 M HF	Ethyl ether	<0.1
Silver	Ag(I)	20 M HF	Ethyl ether	0.05
Tantalum	Ta(V)	10 M HF, 6 M H <sub>2</sub> SO <sub>4</sub> , 2.2 M NH <sub>4</sub> F	Methyl isobutyl ketone <sup>b</sup>	99.6
	Ta(V)	0.4 M HF, 3.7 M HCl	Diisopropyl ketone <sup>b</sup>	81( <sup>a</sup> Ta/Nb=91)
	Ta(V)	0.4 M HF, 3.9 M HNO <sub>3</sub>	Diisopropyl ketone <sup>b</sup>	79( <sup>a</sup> Ta/Nb=880)
	Ta(V)	0.4 M HF, 4.5 M H <sub>2</sub> SO <sub>4</sub>	Diisopropyl ketone <sup>b</sup>	95( <sup>a</sup> Ta/Nb=160)
	Ta(V)	0.4 M HF, 4.6 M HClO <sub>4</sub>	Diisopropyl ketone <sup>b</sup>	90( <sup>a</sup> Ta/Nb=290)
	Ta(V)	20 M HF	Ethyl ether	79.3
Tellurium	Te(IV)	20 M HF	Ethyl ether	23
Thallium	Tl(I)	20 M HF	Ethyl ether	<0.05
Tin	Sn(II)	4.6 M HF	Ethyl ether <sup>a</sup>	100
	Sn(II)	20 M HF	Ethyl ether	4.9
	Sn(IV)	1.2-4.6 M HF	Ethyl ether <sup>a</sup>	100
	Sn(IV)	20 M HF	Ethyl ether	5.2
Titanium	Ti(IV)	20 M HF	Ethyl ether	<0.05
Tungsten	W(VI)	10 M HF, 6 M H <sub>2</sub> SO <sub>4</sub> , 2.2 M NH <sub>4</sub> F	Methyl isobutyl ketone <sup>b</sup>	~26
	W(VI)	20 M HF	Ethyl ether	0.5
Uranium	U(VI)	20 M HF	Ethyl ether	1.1
Vanadium	V(III)	20 M HF	Ethyl ether	12
	V(V)	20 M HF	Ethyl ether	8.5
Zinc	Zn(II)	20 M HF	Ethyl ether	0.9
Zirconium	Zr(IV)	20 M HF	Ethyl ether	2.9

<sup>a</sup>4:1 volume ratio of organic to aqueous phase.<sup>b</sup>Organic phase pre-equilibrated with pure aqueous phase.

TABLE 6. CHLORIDE EXTRACTIONS

Element	Oxidation State	Solvent System (before mixing)		Per Cent Extraction
		Aqueous Phase	Organic Phase	
Antimony	Sb(V)	6 M HCl	Ethyl ether	81
	Sb(V)	6.5-8.5 M HCl	Isopropyl ether	99.5
	Sb(V)	1-2 M HCl, 0.0032 M oxalic acid, 0.0021 M citric acid	Ethyl acetate	83
Arsenic	Sb(III)	6 M HCl	Ethyl ether	6
	Sb(III)	6.5-8.5 M HCl	Isopropyl ether	1.6
	As(V)	6 M HCl	Ethyl ether	2-4
	As(III)	6 M HCl	Ethyl ether	68
Cobalt	As(III)	11 M HCl	Benzene	94
	Co(II)	4.5 M HCl	2-Octanol	9.1 (Co/Ni=70)
	Co(II)	0.85 M CaCl <sub>2</sub>	2-Octanol	9.1 (Co/Ni=10)
Gallium	Ga(III)	6 M HCl	Ethyl ether	97
	Ga(III)	7 M HCl	Isopropyl ether	>99.9
	Ga(III)	3 M HCl	Tributyl phosphate	99.9
<u>Germanium</u>	Ge(IV)	6 M HCl	Ethyl ether	40-60
	Ge(IV)	10.5 M HCl	Carbon tetrachloride	99.5
	Ge(IV)	11 M HCl	Benzene	99.6
Gold	Au(III)	10% HCl	Ethyl acetate	100
	Au(III)	6 M HCl	Ethyl ether	95
	Au(III)	pH 2-6 in HCl, sat. KCl	n-Butyl alcohol	Spot test
Indium	In(III)	8 M HCl	Ethyl ether <sup>a</sup>	3.02
Iron	Fe(III)	6 M HCl	Ethyl ether	99
	Fe(III)	7.75-8.0 M HCl	Isopropyl ether	99.9
	Fe(III)	9 M HCl	<i>β, β'</i> -Dichloroethyl ether	99
	Fe(III)	8 M HCl	Methyl amyl ketone	100
Lithium	Li(I)	Chloride in small volume of water	Amyl alcohol	0.66 g/10 ml
			2-Ethylhexanol	3 g/100 ml
Mercury	Hg(II)	0.125 M HCl	Ethyl acetate	80
	Hg(II)	0.1 M HCl	n-Butyl acetate + tri-chloroacetic acid (3 M)	82-89
Molybdenum	Hg(II)	6 M HCl	Ethyl ether	0.2
	Mo(VI)	6 M HCl	Ethyl ether	80-90
	Mo(VI)	7.75 M HCl	Isopropyl ether	21
	Mo(VI)	5 M HCl	Amyl acetate	99
Nickel	Ni(II)	4.5 M HCl	2-Octanol	0.14 (Co/Ni=70)
	Ni(II)	0.85 M CaCl <sub>2</sub>	2-Octanol	0.99 (Co/Ni=10)
Niobium	Nb(V)	11 M HCl	Diisopropyl ketone <sup>b</sup>	90
Platinum	Pt(II)	3 M HCl, 1 ml of 10% SnCl <sub>2</sub>	Ethyl ether	>95
Polonium	Po(II)	6 M HCl	20% tributyl phosphate	80-90
Protactinium	Pa(V)	6 M HCl, 8 M MgCl <sub>2</sub>	<i>β, β'</i> -Dichloroethyl ether	90
	Pa(V)	6 M HCl	Diisopropylcarbinol <sup>b</sup>	99.9
	Pa(V)	6 M HCl	Diisopropyl ketone	99
Scandium	Sc(III)	8 M HCl	Tributyl phosphate	98
Tellurium	Te(IV)	6 M HCl	Ethyl ether	34
Thallium	Tl(III)	6 M HCl	Ethyl ether	90-95
Tin	Sn(IV)	6 M HCl	Ethyl ether	17
	Sn(II)	6 M HCl	Ethyl ether	15-30
Vanadium	V(V)	7.75 M HCl	Isopropyl ether	22

<sup>a</sup>30:20 volume of organic to aqueous phase.

<sup>b</sup>Organic phase pre-equilibrated with pure aqueous phase.

TABLE 7. EXTRACTABILITY OF METAL THIOCYANATES INTO ETHYL ETHER

Percentage of element extracted from solutions having an initial metal concentration of 0.1 M and 0.5 M HCl; extraction at room temperature using equal volumes of phases.

Element	Molarity of Ammonium Thiocyanate							
	0.5	1	2	3	4	5	6	7
Be(II)		3.8	24.3	49.7		84.1		92.2
Zn(II)		96.0		97.4		94.8		92.8
Co(II)		3.6	37.7	58.2		74.9		75.2
Al(III)				1.1		9.0	19.4	
Sc(III)		12.7	55.4	79.8	84.6			89.0
Ga(III)	18.3	65.4		90.5				99.3
In(III)	26.0	51.5	75.1	75.3		68.3		47.6
Tl(III)	14.7	58.8	80.5	84.0		79.8		76.3
Tl(IV)								13.0
Fe(III)		88.9		83.7		75.5		53.3
Sn(IV)		99.3		99.9		>99.9		>99.9
V(IV)	10.7	15.0	13.1	8.7				2.2
Mo(V)		99.3	97.2					97.3
U(VI)		45.1	41.4	29.4		13.8		6.7
Cu(I)			2.9			0.4		
Ge(IV)		<0.3						<0.5
As(III)		0.4 <sup>a</sup>						0.4 <sup>a</sup>
As(V)		0.1					0.03	
Sb(III)		Hydrolysis		Hydrolysis		Hydrolysis		2.2
Bi(III)		0.3 <sup>b</sup>						0.1
Cd(II)		0.1						0.2 <sup>c</sup>
Cr(III)		0.06 <sup>b</sup>						3.4 <sup>b</sup>
Pd(II)		1.7 <sup>d</sup>						0.1
Ni(II)		0.01 <sup>d</sup>						0.003 <sup>d</sup>
Hg(II)		0.15 <sup>d</sup>						0.15 <sup>d</sup>
Li(I)								0.04 <sup>d</sup>

<sup>a</sup> 0.8 M HCl used.

<sup>b</sup> 10:1 volume ratio of ether to water used.

<sup>c</sup> 6:1 volume ratio of ether to water used.

<sup>d</sup> Neutral aqueous solution extracted with a 10:1 volume ratio of ether to water.

TABLE 8. EXTRACTION PROPERTIES OF CARRIER-FREE CONCENTRATIONS OF FISSION PRODUCT ELEMENTS WITH MIXED BUTYLPHOSPHORIC ACID

Conditions: Aqueous phase, 1 M HNO<sub>3</sub>, 5-minute mixing; volume ratio (organic/aqueous), 1:1.

Concentration of DBPA, <sup>a</sup> M	Elements Extracted		
	<5% by DBPA	5-95% by DBPA	>95% by DBPA
0.06	Cs, Sr, La, Ce(III), Ag, <sup>b</sup> Cd, <u>Ge</u> , Se(IV), Te(IV), Sb(III), <sup>c</sup> Sb(V), As(V), Pd, <sup>b</sup> Ru, Rh, Nb	Y, 15%; Sn(IV), <sup>b</sup> 50%; Mo, <sup>b</sup> 15%	Zr, In
0.6	Cs, Sr, La, Ag, <sup>b</sup> Cd, <u>Ge</u> , Se(IV), Te(IV), Sb(III), <sup>c</sup> Sb(V), As(V), Pd, <sup>b</sup> Ru, Rh	Mo, <sup>b</sup> 23%; Nb, 60%; Ta, <sup>c</sup> 85%	Zr, Nb, <sup>c</sup> Y, In, Sn(IV) <sup>b</sup>

<sup>a</sup> Di-n-butylphosphoric acid solution in which the mole ratio of di-n-butylphosphoric acid to mono-n-butylphosphoric acid is 4.5:1.

<sup>b</sup> Silver, Sn, Pd, and Mo were not carrier-free; their concentrations were 0.5, 3, 8, and 8 μg/ml, respectively.

<sup>c</sup> No H<sub>2</sub>O<sub>2</sub> present.

TABLE 9. EXTRACTION PROPERTIES OF MACRO QUANTITIES OF FISSION  
PRODUCT ELEMENTS WITH MIXED BUTYLPHOSPHORIC ACIDS

Conditions: Aqueous phase, 1 mg element per milliliter, 1 M H<sub>2</sub>SO<sub>4</sub>, 2.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.004 M oxalic acid, 6 % H<sub>2</sub>O<sub>2</sub>; volume ratio (organic/aqueous), 1:1; mixing time, 15 minutes with 0.06 M DBPA and 5 minutes with 0.6 M DBPA.

Concentration of DBPA, <sup>a</sup> M	Elements Extracted		
	<5% by DBPA	5-95% by DBPA	>95% by DBPA
0.06	Cs, Sr, Y, La, Ce(III), Ag, Cd, <u>Ge</u> , Se(IV), Te(IV), Sb(III), <sup>b</sup> Sb(V), As(V), Pd, Ru, Rh, Mo, Nb	Sn(IV), 15%; In, 85%	Zr, I <sub>2</sub>
0.6	Cs, Sr, La, Ce(III), Ag, Cd, <u>Ge</u> , Se(IV), Te(IV), Sb(III), <sup>b</sup> Sb(V), As(V), Pd, Ru, Rh, Mo	Sn(IV), 50%; Ta, 35%	Zr, Nb, <sup>b</sup> Y, Ho, In, I <sub>2</sub>

<sup>a</sup> Di-n-butylphosphoric acid solution in which mole ratio of di-n-butylphosphoric acid to mono-n-butylphosphoric acid is 4.5:1.

<sup>b</sup> No H<sub>2</sub>O<sub>2</sub> present.

These tables are taken from Morrison and Frieser, "Solvent Extraction in Analytical Chemistry," Chapter 11, pp. 125-56, John Wiley and Sons, Inc., 1960, and may be referred to for additional references to the original literature.

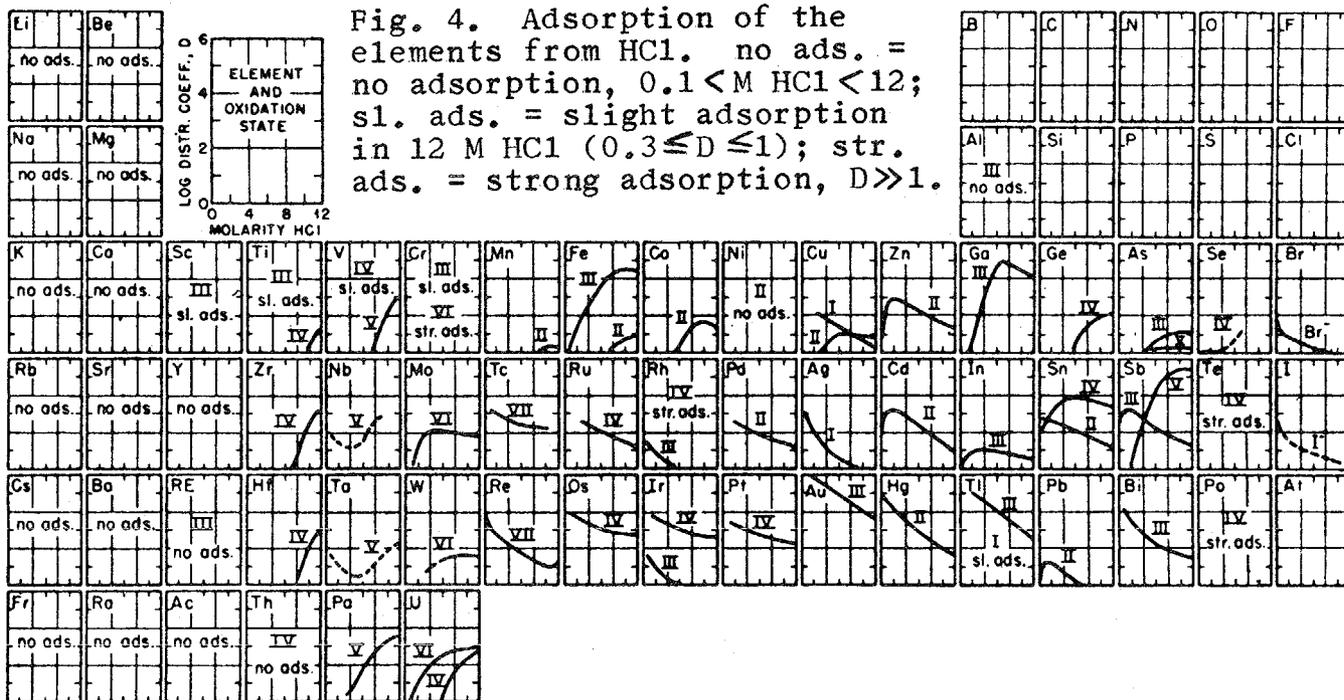
The anion-exchange behavior of germanium in hydrochloric, hydrofluoric and hydrochloric-hydrofluoric acid mixtures has been compared with other elements.<sup>(25,26)</sup> Results of these measurements with the quarternary-amine resin, Dowex-1 are presented in Figures 4 and 5, and the applicability of the ion-exchange technique to the separation of germanium from other elements in these systems can be estimated from their examination.

Results of independent studies of the anion-exchange separation of arsenic (III) and germanium (IV) from phosphorus and arsenic (V) with Dowex-2 are in agreement with the data presented above in Figure 4.<sup>(27)</sup> Arsenic (III) and germanium (IV) are considerably absorbed in the concentration range exceeding 6 M hydrochloric acid whereas phosphorus and arsenic (V) are not significantly absorbed. Above 9 M the quantitative removal of germanium (IV) cannot be achieved presumably due to the insolubility of the tetrachloride in concentrated hydrochloric acid.

The separation of germanium from gallium, indium and antimony as well as other elements by cation-exchange has also been demonstrated.<sup>(28)</sup> Germanium is not retained by Dowex-50 in the hydrogen form at any hydrochloric acid concentration whereas antimony, indium and gallium are absorbed and not readily eluted until concentration values of 0.2, 0.4 and 1.3 M, respectively, are employed.

The anion-exchange resin IRA-411, originally in the chloride or fluoride ion form, has been used to absorb germanium hematoxylin complex from a 0.02 M hydrochloric acid solution.<sup>(29)</sup> Minute amounts of germanium have been concentrated in this manner as a red-colored compound in the resin to provide a method for its detection. Antimony (III), iron and bismuth interfere.

Ion-exchange studies of germanate systems made<sup>(30,31)</sup> primarily to elucidate the chemistry of tetravalent germanium



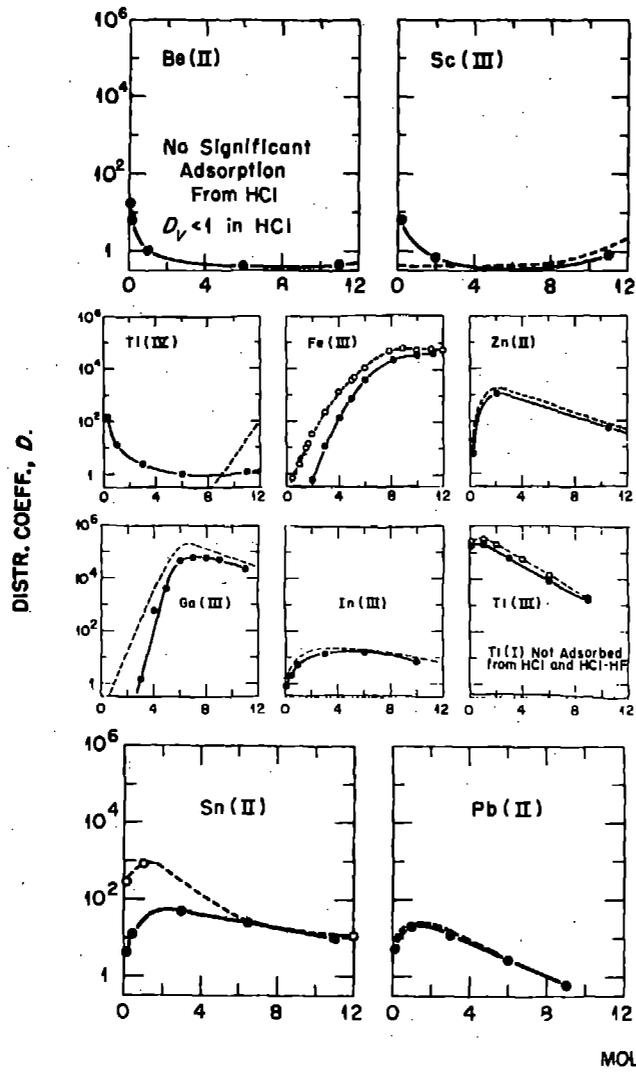
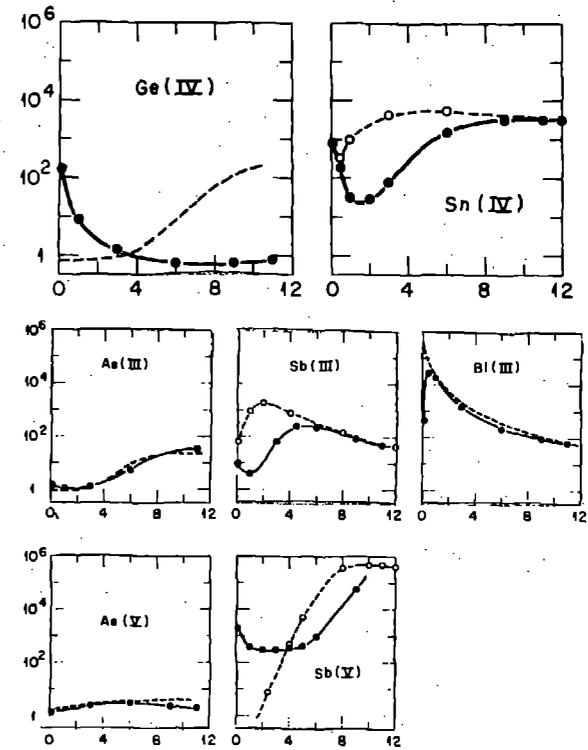


Fig. 5. Anion Exchange Adsorbability in HCl-HF Solutions

(1 M HF); --- and ---○---, HCl; ●---, HCl-HF.



provide additional insight with regard to potential separation procedures for germanium. Only chloride and germanate ions are absorbed from ethylene glycol by Amberlite IRA-400 in the chloride ion form at all pH values between 6 and 12. These ions are absorbed only up to a pH value of 9 from glycerol. At pH values greater than 9 a doubly charged 1:1 monogermanic acid-glycerol complex is absorbed. Solutions containing a germanium-mannitol mole ratio of 1:5 or 1:7 result in the exchange of a singly charged 1:1 monogermanic acid-mannitol complex together with chloride ion at pH values up to 8. A doubly charged 1:2 monogermanic acid-mannitol complex is absorbed above a pH of 10. With solutions containing a germanium-mannitol mole ratio of unity a singly charged monogermanic acid-mannitol complex is exchanged. (30)

Results of ion-exchange studies of germanate solutions as a function of pH and sulfate and orthophosphate ion (31) content indicate (1) the depolymerization of pentavalent germanate ion to monogermanate as pH drops from 9 to 4, the less complex ion being less firmly absorbed and (2) the existence of two complex acids  $[\text{GeO}_2(\text{SO}_4)]^{2-}$  and  $[\text{HGeO}_2(\text{PO}_4)]^{2-}$ .

A micro-technique that is employed for the separation and determination of germanium but does not usually receive attention from the radiochemist because of (1) unfamiliarity with the method and (2) the length of time required for separation is paper chromatography. Separation of germanium is achieved by the development of chromatograms on filter paper with solvent mixtures such as chloroform-ethanol-concentrated hydrochloric acid, butyl alcohol-concentrated hydrochloric acid-water and isobutyl alcohol-hydrochloric acid-water. (32,33,34) Sharp spots due to germanium obtain when developer reagent such as oxidized hematoxylin is added. (33,34) Measurement of the area of the spot permits an accurate estimate of the germanium content of the

sample.<sup>34</sup> Separation of germanium (II) by this method from beryllium, indium and gallium,<sup>(35)</sup> and of germanium (IV) from iron (III)<sup>(32)</sup> as well as additional important elements of the second and third analytical groups<sup>(36)</sup> have been reported.

Application of this technique to the radiochemical separation of germanium seems worthy of consideration by the radiochemist. Measurement of the activity associated with a separated germanium chromatogram can be easily correlated with recovery estimates based, for example, upon measurement of the area of the spot due to micro amounts of germanium originally added to the sample before analysis.

Electrochemical methods may also be employed to provide a preliminary separation of germanium. Germanium is quantitatively extracted from dilute sulfuric acid solution by electrodeposition in a mercury cathode.<sup>(7,37)</sup>

#### 4. Determination of Germanium

Accurate estimate of the recovery of added carrier after separation and purification of the desired element for activity measurement is a requirement of any suitable radiochemical procedure. Radioactivity associated with the desired element must be accurately correlated with its chemical recovery. Precipitation of the element in a reproducibly weighable form is thus of great importance. The precipitate, in addition, must not be so bulky that it interferes with accurate estimate of the radioactivity associated with the element of interest because of self-absorption and -scattering effects.

Germanium, after separation as the sulfide from a fairly acid solution is usually converted to the oxide for weighing by treatment with ammonia and 3% hydrogen peroxide or by hydrolysis

with steam. Evaporation of the solution to dryness at 105°C. is then followed by ignition at 900°C. to constant weight. Direct ignition is avoided because the formation of volatile germanium (II) oxide causes indeterminate losses as is also the case in direct oxidation with nitric acid.

Quadrivalent germanium can be quantitatively precipitated instead as magnesium orthogermanate,  $Mg_2GeO_4$ , in ammoniacal solution free from chloride ion. Any chloride retained in the precipitate will volatilize the germanium during the ignition step. Ammonium tartrate can be added prior to the precipitation with magnesium, ammonium sulfate mixture to prevent coprecipitation of arsenic and phosphorus. A potential source of error in this method, however, is coprecipitation of magnesium hydroxide.

Tannin can be used in the presence of dilute acid to precipitate germanium. Ignition to constant weight at 900°-950°C. converts the precipitate to  $GeO_2$ .<sup>(38)</sup>

Germanium forms the complex  $H_2Ge(C_2O_4)_3$  with oxalic acid and the addition of 5,6 benzoquinoline oxalate to this solution gives a nonstoichiometric precipitate which is ignited to germanium (IV) oxide for weighing.

Regardless of the method used to obtain the germanium (IV) oxide, drying of the precipitate at 100°C. will not remove all of the water and ignition at 900°C. is necessary. During the ignition step reduction to volatile germanium (II) oxide must be avoided when filter paper is present.

The precipitation of salts of molybdo-germanic or tungsto-germanic acid<sup>(39)</sup> by organic bases such as pyridine, cinchonine, 8-quinolinol, or hexamethylenetetramine give weighing forms with more favorable gravimetric factors<sup>(40)</sup> than  $GeO_2$  upon conversion to their constant composition forms at elevated temperatures.

The temperature limits within which the different gravimetric forms discussed above have constant composition<sup>(41)</sup> are summarized in the following Table.

TABLE 10. EFFECT OF TEMPERATURE ON GRAVIMETRIC FORMS

Reagent	Precipitate	Gravimetric Form	Temp. Range of Constant Composition (°C)
H <sub>2</sub> S	GeS <sub>2</sub>	GeO <sub>2</sub>	410 - 946
Mg <sup>2+</sup>	Mg <sub>2</sub> GeO <sub>4</sub>	Mg <sub>2</sub> GeO <sub>4</sub>	280 - 814
Tannin	Ge tannate	GeO <sub>2</sub>	900 - 950
-naphthoquinoline plus oxalic acid	B <sub>2</sub> Ge(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub>	GeO <sub>2</sub>	above 800
hexamethylene-tetramine	B <sub>4</sub> GeMo <sub>12</sub> O <sub>40</sub>	GeO <sub>2</sub> ·12MoO <sub>3</sub>	440 - 813
pyridine	B <sub>4</sub> GeMo <sub>12</sub> O <sub>40</sub>	GeO <sub>2</sub> ·12MoO <sub>3</sub>	429 - 813
oxine	B <sub>4</sub> GeMo <sub>12</sub> O <sub>40</sub>	GeO <sub>2</sub> ·12MoO <sub>3</sub> ·B <sub>4</sub>	50 - 115

Gravimetric methods for the determination of germanium using phenylfluorone<sup>(42)</sup> and 5,7 dibromo -8 hydroquinoline reacted with germanium dodecamolybdic acid<sup>(43)</sup> have also been reported.

The necessity for igniting the final precipitate to assure a reproducibly weighable germanium compound is a definite disadvantage to the radiochemist. Mounting the ignited sample uniformly and reproducibly for beta activity measurement is of course possible but is an annoyance, is time consuming and is a potential source of error as well. The precipitate due to oxine (GeO<sub>2</sub>·12MoO<sub>3</sub>·4C<sub>9</sub>H<sub>7</sub>ON) can be dried in the oven at ~110° directly after filtration and would for this reason appear to be the most useful weighing form for the radiochemist. (The disulfide is used.)

The isolation of essentially carrier-free samples for beta activity measurement is of considerable advantage to the radiochemist since error due to self-absorption and self-scattering effects is nearly eliminated. Analytical methods for the ac-

curate determination of micro-amounts of an element, however, are needed to assure the success of this type of approach. Two such analytical methods for quantitative assay of trace amounts of metal are polarography and colorimetry: The accurate assay of small amounts of germanium for the evaluation of chemical recovery in an aliquot portion of the radiochemically treated sample can be achieved by these analytical techniques even after the addition of almost trace amounts of carrier at the start of a separation. Sample preparation for activity measurement can then consist of evaporation of the purified germanium sample just after extraction into a volatile organic solvent.

Even if the gamma radiation of a sample is to be measured in a scintillation counter arrangement thereby minimizing errors to which beta radiation measurements are susceptible, accurate assay of carrier recovery by these methods is an advantage since the analysis is shortened by elimination of the time-consuming gravimetric procedures.

The yellow color of the molybdo-germanium complex<sup>(44)</sup> is the basis of a colorimetric method of analysis for germanium. It follows Beer's law in concentrations up to 40 ppm and comparison with known color standards permits estimation of quantities of germanium as small as 1 ppm. Phosphates and silicates interfere with the determination.

Reduction of the molybdo-germanium to molybdenum blue increases the sensitivity of this colorimetric method,<sup>(45,46)</sup> Beer's law holding in the range from 0 - 4 ppm. The sensitivity of the colorimetric determination of germanium as molybdo-germanic acid is also increased by the addition of diphenylcarbozone<sup>(47)</sup> as little as 0.1% of germanium being detectable in 0.03 ml. of solution. Acidifying the purple solution that forms with hydrochloric or sulfuric acid imparts a blue color. Phosphate and arsenate ions lower the sensitivity of the method and fluoride,

tartrate, colored, oxidizing and reducing ions must be removed for successful application of this modification of the colorimetric method. Reaction of ascorbic acid with molybdate at pH 5 prior to reduction to molybdenum blue has been employed for this colorimetric determination of germanium also.<sup>(48)</sup>

Oxidized hematoxylin forms a purple complex with germanium and is applicable for the analysis of 0.08 to 1.6 ppm of germanium.<sup>(49)</sup> The advantage of this method is that other elements forming heteropolyacids do not interfere.

The pink phenylfluoronegermanium complex<sup>(50,51)</sup> follows Beer's law for amounts up to 1 ppm of germanium. It is suitable for the determination of 5 to 50 ug of germanium.<sup>(21)</sup> Improved color development with phenylfluorone has been achieved by the use of an acetate buffer at pH 3.1 rather than strong acid. After color development the acidity is increased to destroy interfering metal fluorone complexes. Ethylenediaminetetracetic acid is beneficially employed to suppress interferences due to a number of metals. Interference due to antimony is eliminated by oxidation to antimony (V) with perchloric acid and hydrogen peroxide addition prevents interference by molybdenum and niobium.<sup>(52)</sup> With a 0.05% ethanol solution of 2,6,7-trihydroxy-9-(4-dimethylaminophenyl) fluorone (phenylfluorone) germanium concentrations of 0.05 to 1.2 ppm in 0.5 M hydrochloric acid can be determined. Tin (IV), antimony (III), zirconium (IV), cerium (IV), iron (III) and permanganate ions are believed to interfere.<sup>(53)</sup>

Germanium, recovered as trioxalatogermanic acid, can be determined colorimetrically with quinalizarin acetate in an ammonium oxalate-oxalic acid solution buffered to a pH value of 5.<sup>(20)</sup> Arsenic, lead, iron, phosphorus, silicon, magnesium, aluminum, nickel, mercury (II), manganese, zinc, uranium and vanadium do not interfere. Acetate and tartrate ions decrease the color intensity of the complex. The method is applicable

in the range of 1 to 100  $\gamma$  of germanium and methanol must be added for concentrations of germanium greater than 5 $\gamma$  to prevent precipitation of the complex.<sup>(54)</sup>

Germanium combines with quercetin to form a yellow-green complex. Optimum results are obtained in 40% methanol solution buffered with phosphate to a pH value of 6.7 - 7.1. Beer's law is obeyed up to a germanium concentration level of 0.54 $\gamma$  per ml.<sup>(17)</sup> Arsenic and selenium do not interfere.

A fluorometric determination of trace amounts of germanium is based upon the intense greenish-yellow fluorescence that is emitted when a solution of resacetophenone in concentrated sulfuric or sirupy phosphoric acid added to a germanium containing solution is exposed to ultraviolet radiation. No other metals are believed to interfere.<sup>(55)</sup>

Practical polarographic determination of germanium at a concentration level of  $10^{-4}$  M (3 ppm) has been shown to be feasible provided that the element is first reduced to the 2+ state with hypophosphite in hydrochloric acid. Elements such as arsenic, lead and tin which produce waves in the vicinity of -0.4 v interfere with the germanium wave.

Another polarographic procedure of analytical utility makes use of the anodic wave that is obtained in acidic solution at -0.130 volts with germanium (II) produced by prior reduction of germanium (IV) with sodium hypophosphite.<sup>(56)</sup> Chloride ion, which interferes by affecting the height of the wave, can be removed by complexing with excess cadmium sulfate. Metals ordinarily present with germanium do not interfere with determinations down to  $10^{-6}$  M (.03 ppm) germanium (IV) if conditions are carefully regulated.

The use of .1 M ethylenediaminetetracetic acid as supporting

electrolyte has been claimed to permit the determination of 8 ug to 1 mg of germanium polarographically.<sup>(57)</sup>

Advantage has also been taken of the property of germanium to form the well-defined germanomolybdic acid, molybdenum being determined polarographically to estimate germanium content.<sup>(58)</sup>

#### V. DISSOLUTION OF MATERIALS CONTAINING GERMANIUM

The basis for most of the methods designed for the extraction of germanium from its ores or its several stable compounds consists of reacting the solid with concentrated hydrochloric acid and collecting the distillate as volatile germanium tetrachloride.

If volatilization of germanium tetrachloride is undesirable it can be suppressed when attack of the compound with hydrochloric acid, aqua regia, mixtures of sulfuric acid or perchloric acid with hydrochloric or hydrobromic acids is performed in the presence of hydrofluoric acid.

Germanium compounds can also be broken up by fusion with sodium carbonate and sulfur for extraction with water. Other methods of alkaline extraction use 50% sodium hydroxide or sodium peroxide.

Germanium metal is dissolved by three percent hydrogen peroxide.

#### VI. RADIOASSAY TECHNIQUES FOR GERMANIUM

Surveys of general methods for the measurement of radioactive sources are available in the literature.<sup>(59,60)</sup> The techniques of gamma-ray scintillation spectrometry have also been adequately described.<sup>(61,62)</sup> The state of counting technology is such that the determination of absolute disintegration rates can be achieved by  $4\pi$  beta counting methods<sup>(63,64)</sup> or from

absolute calibration of scintillation crystals<sup>(65)</sup> if the gamma and beta decay scheme for a particular nuclide is known.

The nuclear characteristics of the various germanium nuclides are summarized in Section II of this monograph. The standard methods of beta and gamma activity measurement may be employed for radiochemical assay of most of the germanium nuclides when appropriate consideration of these data are made. Selection of a method of activity measurement for each nuclide must be based upon its half-life, the nature and energy of the radiations characterizing its decay, and its scheme of decay.

For example, the 1.5 m Ge<sup>65</sup> decays by energetic positron and gamma ray emission and may be assayed with a Geiger, proportional or scintillation counter. No attempt to determine the absolute disintegration rate of this nuclide can be made, however, until its decay scheme has been extensively studied and is well understood. The 11.4 d Ge<sup>71</sup> decays by electron capture and is detectable only through the observation of x-rays in a scintillation counter. Isomerism occurs in Ge<sup>75</sup> and Ge<sup>77</sup> and genetic relationships must be considered in their radioactive assay. The beta and gamma ray spectra associated with the decay of these nuclides are complex and internal conversion of the gamma transitions due to the isomers complicate analysis even though gross radiochemical assay can be easily achieved by standard beta and gamma counting techniques. Gamma ray spectrometry resolves this problem, the activity assay being based upon the detection of a predominant gamma ray of known relative intensity.

## VII. ACTIVATION ANALYSIS FOR GERMANIUM

Activation analysis may be considered to be a useful technique for the determination of trace amounts of germanium. Data for

experimental methods and for nuclear reactions applicable or potentially applicable to the analysis of trace amounts of germanium by activation methods are presented below and are from the "Activation Analysis Handbook," authored by R. C. Koch, Academic Press, New York and London, 1960. For references to the original literature consult pages 86 and 87 of this text.

Table 11. Evaluation of Neutron Reactions

$\text{Ge}^{70}(\text{n},\gamma)\text{Ge}^{71}$	Possible interference from $\text{Se}^{74}(\text{n},\alpha)\text{Ge}^{71}$ with a Se matrix; possible interference from second-order reaction: $\text{Ga}^{69}(\text{n},\gamma)\text{Ga}^{70} \xrightarrow{\gamma} \text{Ge}^{70}(\text{n},\gamma)\text{Ge}^{71}$ .
$\text{Ge}^{74}(\text{n},\gamma)\text{Ge}^{75}$	Possible interference from $\text{As}^{75}(\text{n},\text{p})\text{Ge}^{75}$ with an As matrix; from $\text{Se}^{78}(\text{n},\alpha)\text{Ge}^{75}$ with a Se matrix.
$\text{Ge}^{76}(\text{n},\gamma)\text{Ge}^{77}$	Possible interference from $\text{Se}^{80}(\text{n},\alpha)\text{Ge}^{77}$ with a Se matrix; from fission of U or Pu.
$\text{Ge}^{70}(\text{n},\text{p})\text{Ga}^{70}$	Possible interference from $\text{Ga}^{69}(\text{n},\gamma)\text{Ga}^{70}$ or $\text{Ga}^{71}(\text{n},2\text{n})\text{Ga}^{70}$ ; possible interference from secondary reaction: $\text{Zn}^{70}(\text{p},\text{n})\text{Ga}^{70}$ .
$\text{Ge}^{72}(\text{n},\text{p})\text{Ga}^{72}$	Possible interference from $\text{Ga}^{71}(\text{n},\gamma)\text{Ga}^{72}$ ; from $\text{As}^{75}(\text{n},\alpha)\text{Ga}^{72}$ ; from fission of Th, U, or Pu.
$\text{Ge}^{73}(\text{n},\text{p})\text{Ga}^{73}$	No apparent interference at $E < 20$ Mev.
$\text{Ge}^{74}(\text{n},\alpha)\text{Zn}^{71}$	Possible interference from $\text{Zn}^{70}(\text{n},\gamma)\text{Zn}^{71}$ ; from $\text{Ga}^{71}(\text{n},\text{p})\text{Zn}^{71}$ .
$\text{Ge}^{70}(\text{n},2\text{n})\text{Ge}^{69}$	No apparent interference from primary reactions at $E < 20$ Mev; possible interference from secondary reaction: $\text{Ga}^{69}(\text{p},\text{n})\text{Ge}^{69}$ .
$\text{Ge}^{76}(\text{n},2\text{n})\text{Ge}^{75}$	Possible interference from $\text{As}^{75}(\text{n},\text{p})\text{Ge}^{75}$ ; from $\text{Se}^{78}(\text{n},\alpha)\text{Ge}^{75}$ .

Table 11. (Continued)

## Standard Sensitivities

$\text{Ge}^{70}(\text{n}, \gamma)\text{Ge}^{71}$	$3 \times 10^{-5} \mu\text{g.}$
$\text{Ge}^{74}(\text{n}, \gamma)\text{Ge}^{75+75\text{m}}$	$2 \times 10^{-4} \mu\text{g.}$
$\text{Ge}^{76}(\text{n}, \gamma)\text{Ge}^{77+77\text{m}}$	$2 \times 10^{-3} \mu\text{g.}$

## Nuclear Data and Analysis Methods for Charged Particle or Photon Activation

## Charged Particle and Photon Activation Analysis Methods

$\text{Ge}^{74}(\text{p}, \text{n})\text{As}^{74}$	Thick-target yield at 22 Mev = 50 mc/ $\mu\text{a-hr.}$
$\text{Ge}(\text{d}, \quad)\text{As}^{71}$	Thick-target yield at 15 Mev = 7.6 $\mu\text{c}/\mu\text{a-hr.}$
$\text{Ge}(\text{d}, \quad)\text{As}^{72}$	Thick-target yield at 15 Mev = 64.9 $\mu\text{c}/\mu\text{a-hr.}$
$\text{Ge}(\text{d}, \quad)\text{As}^{73}$	Thick-target yield at 15 Mev = 1.1 $\mu\text{c}/\mu\text{a-hr.}$
$\text{Ge}(\text{d}, \quad)\text{As}^{74}$	Thick-target yield at 15 Mev = 5.2 $\mu\text{c}/\mu\text{a-hr.}$

## Evaluation of Charged Particle and Photon Reactions

$\text{Ge}^{74}(\text{p}, \text{n})\text{As}^{74}$	Possible interference from $\text{Se}^{77}(\text{p}, \alpha)\text{As}^{74}$ ; from $\text{As}^{75}(\text{p}, \text{pn})\text{As}^{74}$ at $E > 12$ Mev; possible interference from secondary reaction: $\text{Se}^{74}(\text{n}, \text{p})\text{As}^{74}$ .
$\text{Ge}(\text{d}, \quad)\text{As}^{74}$	Possible interference from $\text{Se}^{76}(\text{d}, \alpha)\text{As}^{74}$ ; from $\text{As}^{75}(\text{d}, \text{dn})\text{As}^{74}$ ; possible interference from secondary reactions: $\text{Se}^{74}(\text{n}, \text{p})\text{As}^{74}$ ; $\text{Se}^{77}(\text{p}, \alpha)\text{As}^{74}$ .
$\text{Ge}(\text{d}, \quad)\text{As}^{73}$	Possible interference from $\text{Se}^{76}(\text{d}, \alpha\text{n})\text{As}^{73}$ ; possible interference from secondary reaction: $\text{Se}^{76}(\text{p}, \alpha)\text{As}^{73}$ .
$\text{Ge}(\text{d}, \quad)\text{As}^{72}$	Possible interference from $\text{Se}^{74}(\text{d}, \alpha)\text{As}^{72}$ with a Se matrix.
$\text{Ge}(\text{d}, \quad)\text{As}^{71}$	Possible interference from $\text{Se}^{74}(\text{d}, \alpha\text{n})\text{As}^{71}$ with a Se matrix.

TABLE 12

## Nuclear Data and Analysis Methods for Neutron Activation of GERMANIUM

Reactor Neutron Reaction Data					
Isotope	Abundance (percent)	Cross-section (barns)	Half-life of Activation Product	Principal Beta Radiations	Principal Gamma Radiations
Ge <sup>70</sup>	20.55	3.4 ± 0.3 3.9 ± 1.2 a	11.4 d	EC	none
Ge <sup>72</sup>	27.37	0.98 ± 0.09	stable		
Ge <sup>73</sup>	7.67	14 ± 1	stable		
Ge <sup>74</sup>	36.74	0.62 ± 0.06 40 ± 8 mb a 0.21 ± 0.08 a	48 s 82 m	1.14(85) 0.614(15)	IT(100) M
Ge <sup>76</sup>	7.67	0.36 ± 0.07 80 ± 20 mb a 80 ± 20 mb a	54 s 11.3 h	2.7(86)	IT(14) M

$R = 3.5 \pm 2.9$   
 = resonance integral, absorption  
 $\sigma_a$  = activation  $\sigma$   
 $\sigma$  = absorption  $\sigma$

Mev (%)  
 EC (%) = electron capture  
 M = multiple gammas  
 IT(%) = isomeric transition

## Neutron Activation Analysis Methods

Ge<sup>74</sup>(n,  $\gamma$ )Ge<sup>75</sup> Determination of Ge with a calculated sensitivity of 0.04  $\mu$ g; flux =  $5 \times 10^{11}$ .

Ge<sup>76</sup>(n,  $\gamma$ )Ge<sup>77</sup> Determination of Ge with a sensitivity of 0.4  $\mu$ g; flux =  $5 \times 10^{11}$ .

## Data for Other Neutron Reactions

Ge <sup>70</sup> (n, p)Ga <sup>70</sup>	$E_{th} = 1.8$ Mev; $\sigma(14.5) = 0.13$ b.
Ge <sup>72</sup> (n, p)Ga <sup>72</sup>	$\sigma(14.5) = 65$ mb.
Ge <sup>73</sup> (n, p)Ga <sup>73</sup>	$\sigma(14.5) = 0.14$ b.
Ge <sup>74</sup> (n, $\alpha$ )Zn <sup>71</sup>	$\sigma(14.5) = 14.9$ mb.
Ge <sup>70</sup> (n, 2n)Ge <sup>69</sup>	$\sigma(14.5) = 0.67$ b.
Ge <sup>76</sup> (n, 2n)Ge <sup>75</sup>	$\sigma(14.5) = 1.82$ b.

## VIII. COLLECTED RADIOCHEMICAL PROCEDURES

### Procedure 1

Source "Procedure for the Isolation of Germanium and Arsenic Activities in Fission"

L. Winsberg

Paper 228 in "Radiochemical Studies: The Fission Products" edited by C. D. Coryell and N. Sugarman McGraw-Hill Book Co., Inc., New York (1951)

A procedure based on the successive distillation of  $\text{GeCl}_4$  and  $\text{AsCl}_3$  with  $\text{HCl}$  is given for the isolation of germanium and arsenic activities in fission. Effective decontamination to produce high radioactive purity is obtained.

#### 1. INTRODUCTION

To study the occurrence of short-lived germanium and arsenic activities formed in fission, a procedure was developed for radiochemical separation of these elements from the other fission products. Because of the low fission yields of the isotopes of these elements and the necessity of working with freshly irradiated uranium, a decontamination factor of about  $10^6$  was essential.

#### 2. DISCUSSION

Germanium tetrachloride and arsenic trichloride are distilled readily from conc.  $\text{HCl}$  solution. The germanium and arsenic sulfides are first separated from uranyl nitrate solution and are then redissolved in  $\text{NH}_4\text{OH}$ . A  $\text{Zr}(\text{OH})_4$  scavenging at this point removes many other  $\text{H}_2\text{S}$ -insoluble ions in addition to zirconium, niobium (columbium), and the rare earths. Germanium tetrachloride is distilled in an atmosphere of  $\text{Cl}_2$  gas which serves to retain the arsenic in the nonvolatile pentavalent state. Arsenic trichloride is distilled from a  $\text{HCl}$  solution of  $\text{CuCl}$  which keeps the arsenic in the trivalent state.

In a separation of germanium and arsenic activities by this procedure, 40h  $\text{As}^{77}$  was obtained in more than 90 per cent purity, as shown by a decay curve indicating a decontamination factor of more than  $10^6$ . A second decay curve of 2.1h  $\text{Ge}^{(78)}$  showed that this isotope was obtained in more than 99 per cent purity, indicating a decontamination factor of more than  $10^5$  for this element.

#### 3. PROCEDURE

Step 1. To an appropriate amount of neutron-irradiated uranyl nitrate solution in a 50-ml centrifuge tube, add 2 ml each of standardized germanium and arsenic carrier solutions

(Note 1) and boil nearly to dryness to remove excess  $\text{HNO}_3$ . Take up in 15 ml of 6N  $\text{HCl}$ , place in an ice bath, and pass in  $\text{H}_2\text{S}$  (Note 2). Centrifuge, and discard the supernatant solution. Wash with 10 to 15 ml of 6M  $\text{H}_2\text{SO}_4$  saturated with  $\text{H}_2\text{S}$ .

Step 2. Dissolve the mixed sulfides of germanium and arsenic in 1 ml of conc.  $\text{NH}_4\text{OH}$ , and dilute to 10 ml. Add 0.5 ml of zirconium carrier solution. Centrifuge, and discard the  $\text{Zr}(\text{OH})_4$  precipitate. Add 10 ml of conc.  $\text{HCl}$  and pass in  $\text{H}_2\text{S}$ . Centrifuge,

PROCEDURE 1 (Continued)

and wash the precipitate with 10 to 15 ml of  $H_2SO_4 - H_2S$  solution. Add 5 ml of  $H_2O$  and heat to expel excess  $H_2S$ . Add 1 ml of conc.  $NH_4OH$  to dissolve any  $GeS_2$  or  $As_2S_3$  remaining, and transfer to a still. Add 10 mg each of tellurium, antimony, and tin carriers. (Disregard the sulfides that form in the still.)

Step 3. Add 10 ml of conc.  $HCl$ , pass in  $Cl_2$  gas, and distill all but 5 ml of the solution into a centrifuge tube containing 5 ml of  $H_2O$  cooled in an ice bath. Set aside the distillate for germanium separation in step 8.

Step 4. Add 5 ml of conc.  $HCl$  and 1 ml of germanium carrier solution, and distill  $GeCl_4$  again, as described in step 3.

Step 5. Remove the  $Cl_2$  gas and pass in air. Add 1 ml of a saturated solution of  $CuCl$  in conc.  $HCl$  and 5 ml of conc.  $HCl$ , and distill to about 1 ml (Note 3). Add 5 ml of conc.  $HCl$  and 1 ml of  $CuCl - HCl$  solution, and distill again to about 1 ml (Note 3). Catch the distillates in 10 ml of  $H_2O$  in a centrifuge tube cooled in an ice bath.

Step 6. Pass  $H_2S$  into the combined distillate to precipitate  $As_2S_3$ . Centrifuge, dissolve in 1 ml of  $NH_4OH$ , add 10 mg each of tellurium, antimony, and tin, and distill as described in step 5.

Step 7. Precipitate the arsenic in the distillate as  $As_2S_3$ , dissolve in 1 ml of conc.  $NH_4OH$ , dilute to 10 ml (Note 4), and add 10 ml of conc.  $HCl$ . Pass in  $H_2S$  to complete the precipitation and then filter through a weighed filter-paper disk. Wash several times with  $H_2O$ , ethyl alcohol, and ether. Heat in an oven at  $110^\circ C$  for 10 min. Weigh as  $As_2S_3$ .

Step 8. Pass  $H_2S$  gas into the distillate obtained in step 3. Centrifuge, and then dissolve the  $GeS_2$  in 1 ml of conc.  $NH_4OH$ . Transfer to a still, add 10 mg each of arsenic, tellurium, antimony, and tin carriers, and distill as outlined in step 3.

Step 9. Precipitate  $GeS_2$ , dissolve in conc.  $NH_4OH$ , add 10 ml of  $H_2O$  (Note 4) and 8 ml of conc.  $HCl$ , and pass in  $H_2S$  to complete the precipitation of  $GeS_2$ . Centrifuge, wash, and mount as described in step 7 for arsenic. Weigh as  $GeS_2$ .

Notes: 1. The germanium carrier solution (germanium concentration of 10 mg/ml) is prepared by dissolving an appropriate amount of germanium metal in a solution of 5 parts conc.  $HCl$  to 1 part conc.  $HNO_3$  under reflux. The arsenic carrier solution (arsenic concentration of 10 mg/ml) is prepared by dissolving  $As_2O_3$  in 6N  $HNO_3$ .

2. Several crystals of  $NH_4I$  may aid precipitation of the sulfides.

3. Take care not to heat to dryness. At higher temperatures antimony distills.

4. If a precipitate remains, centrifuge, and discard the precipitate.

## PROCEDURE 2

### Source "The Separation of Germanium and Arsenic from a Fission-Product Solution"

R. J. Prestwood  
AEC-LA 1721 (December 1954)

#### 1. INTRODUCTION

It is sometimes necessary to isolate both radioarsenic and radiogermanium from the same sample. The separation and isolation of these elements is readily accomplished by utilizing the difference in ease of extraction of germanium (IV) and arsenic (III) iodides into chloroform in the presence of hydriodic acid.

#### 2. REAGENTS

As(V) carrier: 10 mg. As/ml. (added as  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ )  
Ge(IV) carrier: see Procedure 4.  
HCl: conc.  
 $\text{H}_2\text{SO}_4$ : 1M  
 $\text{HClO}_4$ : 4M  
HI: 47%  
Chloroform

#### 3. EQUIPMENT

125-ml separatory funnels (four per sample)  
40-ml conical centrifuge tubes: Pyrex 8320 (one per sample)

#### 4. PROCEDURE

Step 1. To the sample (Note 1) in a 125-ml separatory funnel, add 2.0 ml of As(V) carrier (Note 2) and 2.0 ml of Ge(IV) carrier. (See germanium procedure 4 for the preparation of carrier.) Make the solution 3M in HCl in a total volume of 10 to 15 ml. Add 3 to 4 ml of 47% HI and 20 ml of  $\text{CHCl}_3$  and shake thoroughly. (The As is completely extracted into the  $\text{CHCl}_3$  and the Ge remains in the aqueous phase.) Drain the  $\text{CHCl}_3$  layer into a clean separatory funnel. To the aqueous layer add an additional 10 ml of  $\text{CHCl}_3$  and extract again. Combine the  $\text{CHCl}_3$  extracts. The  $\text{CHCl}_3$  extracts containing  $\text{AsI}_3$  are saved for analysis of arsenic.

Step 2. To the original aqueous layer (which contains the Ge) add 20 ml of 47% HI and extract with 20 ml of  $\text{CHCl}_3$ . Drain the  $\text{CHCl}_3$  layer (which now contains the Ge as  $\text{GeI}_4$ ) into a clean separatory funnel. Extract the aqueous layer again with 10 ml of  $\text{CHCl}_3$  and combine the extracts.

Step 3. Wash the  $\text{CHCl}_3$  containing the  $\text{GeI}_4$  with 10 ml of 4M  $\text{HClO}_4$ . (This removes any  $\text{AsI}_3$  which is present, with a loss of 1% or less of  $\text{GeI}_4$ .) Drain the  $\text{CHCl}_3$  layer into a clean separatory funnel and discard the aqueous phase. The  $\text{CHCl}_3$  containing the  $\text{GeI}_4$  is now treated as in Steps 6-10 of procedure 4.

Notes: 1. The original solution must not contain appreciable quantities of  $\text{NO}_3^-$  ion, otherwise some of the HI which is added will be oxidized to  $\text{I}_2$ .

2. As (V) carrier is used so that reduction to the tri-positive state may promote exchange between active and inactive species.

## PROCEDURE 3

Source "The Separation of Germanium and Arsenic  
from a Fission-Product Solution"

R. J. Prestwood

AEC-LA 1721 (December 1954)

### 1. INTRODUCTION

Arsenic (III) is separated from germanium (IV) by precipitation as the sulfide in hydrochloric acid medium containing fluoride ion, the latter strongly complexing germanium (IV) as  $\text{GeF}_6^-$  and preventing its precipitation. Prior to the sulfide precipitation arsenic (V) is reduced to the tripositive state by means of iodide ion.

### 2. REAGENTS

As (V) carrier: 10 mg. As/ml. (added as  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ )  
Ge (IV) carrier: see Procedure 4.  
HCl: 6M  
HF: conc.  
 $\text{H}_3\text{BO}_3$ : saturated solution  
 $\text{H}_2\text{S}$ : gas  
NaI: solid  
Aerosol: 0.1% in  $\text{H}_2\text{O}$

### 3. EQUIPMENT

40-ml conical centrifuge tubes: Pyrex 8320 (two per sample)  
2", 60° filter funnel (one per sample)  
Centrifuge  
Fisher burner  
Pipets: assorted sizes  
No. 40 Whatman filter paper (9 cm)

### 4. PROCEDURE

Step 1. To the fission-product solution in a 40-ml conical centrifuge tube, add 2.0 ml each of As (V) and Ge (IV) carriers. Make the solution 3 to 5M in HCl and the volume to 10 to 15 ml. (Nitrate ion should be absent, or present only in small amount.) Add 50 to 100 mg of NaI and warm the solution gently. Add 10 drops of conc. HF and saturate the solution with  $\text{H}_2\text{S}$  until the  $\text{As}_2\text{S}_3$  precipitate has coagulated (time required is 3 to 5 min). Centrifuge and pour the supernate through a No. 40 Whatman filter in a 2", 60° funnel into a clean centrifuge tube. The  $\text{As}_2\text{S}_3$  precipitate is then saved for the eventual analysis of arsenic.

Step 2. To the filtrate containing the germanium, add 5 to 6 ml of saturated  $\text{H}_3\text{BO}_3$  and saturate with  $\text{H}_2\text{S}$ . Centrifuge the  $\text{GeS}_2$  precipitate and discard the supernate. The  $\text{GeS}_2$  is then treated as in Step 7 of germanium procedure 4 up through the point at which the germanate solution is made just acidic with HCl. Then the regular germanium procedure is carried out in its entirety (except for the addition of Ge (IV) carrier).

## PROCEDURE 4

Source "Germanium"  
R. J. Prestwood  
AEC-LA 1721 (December 1954)

### 1. INTRODUCTION

In the separation of radiogermanium from other fission products, acid sulfide, lanthanum fluoride, and barium sulfate scavengings are performed in the presence of fluoride ion which keeps germanium in solution as the  $\text{GeF}_6^-$  ion. The fluo complex is then destroyed and germanium distilled as the tetrachloride in a specially designed multiple still. Germanium is finally precipitated and mounted as the sulfide  $\text{GeS}_2$ . The chemical yield is 80 to 90% and the analysis of samples in quadruplicate requires about four hours.

### 2. REAGENTS

Ge (IV) carrier: 10.00 mg Ge/ml - see Preparation of Carrier  
As Carrier: 10 mg As/ml (added as  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ )  
Ba Carrier: 10 mg Ba/ml (added as  $\text{Ba}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$ )  
La Carrier: 10 mg La/ml (added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ )  
Cu Carrier: 10 mg Cu/ml (added as  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$ )  
Zr Carrier: 10 mg Zr/ml (added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in  $1\text{M}$   $\text{HNO}_3$ )  
HCl: 4.5 - 5.5M  
HCl: conc.  
HI: 47% aqueous solution  
 $\text{H}_2\text{SO}_4$ : conc.  
HF: conc.  
 $\text{H}_3\text{BO}_3$ : saturated solution  
 $\text{NH}_4\text{OH}$ : conc.  
 $\text{H}_2\text{S}$ : gas  
 $\text{CH}_3\text{OH}$ : anhydrous

### 3. EQUIPMENT

Fisher burner  
Drying oven  
Centrifuge  
Block for holding centrifuge tubes  
Mounting plates  
Forceps  
Pipets: assorted sizes  
50-ml beakers (two per sample)  
Ground-off Hirsch funnels: Coors 000A (one per sample)  
Filter chimneys (one per sample)  
Filter flasks  
No. 40 Whatman filter paper (9 cm)  
No. 42 Whatman filter circles: 7/8" diameter-weighed  
2", 60° funnels (four per sample)  
40-ml conical centrifuge tubes: Pyrex 8320 (two per sample)  
125-ml Erlenmeyer flask (five per sample)  
Stirring rods  
Oil bath (10" x 4" x 4")  
Special multiple still

## PROCEDURE 4 (Continued)

### 4. PREPARATION OF CARRIER

Fuse 14.4092 gm of c.p.  $\text{GeO}_2$  with 30 gm. of  $\text{Na}_2\text{CO}_3$ . Dissolve the melt in  $\text{H}_2\text{O}$  and dilute to 1 liter. Permit to stand for 24 hours and filter. The solution contains 10.00 mg Ge/ml and is used as a primary standard.

### 5. PROCEDURE

Step 1. To the sample in a 125-ml Erlenmeyer flask add the following: 2.0 ml of standard Ge carrier; 1 ml of As carrier; 1 ml of Ba carrier; 1 ml of Cu carrier; 1 ml of La carrier; 2 ml of 47% HI solution; and 1 ml of conc. HF. Make the solution neutral by the addition of conc.  $\text{NH}_4\text{OH}$ , add 10-20 drops of conc.  $\text{H}_2\text{SO}_4$ , place on a steam bath, and saturate with  $\text{H}_2\text{S}$  for a few minutes.

Step 2. Filter into a clean 125-ml Erlenmeyer flask through No. 40 Whatman filter paper in a 2", 60° funnel. Wash the precipitate with a small quantity of water. Discard the precipitate.

Step 3. To the filtrate add 10 drops of La and 1 ml of Cu carriers and saturate with  $\text{H}_2\text{S}$  on a steam bath. Filter as in Step 2 and wash the precipitate.

Step 4. To the filtrate add 1 ml of Cu carrier and saturate with  $\text{H}_2\text{S}$  in the cold. Filter as in Step 2 and wash the precipitate.

Step 5. Repeat Step 4.

Step 6. To the filtrate add 10 ml of conc. HCl and 10 ml of saturated  $\text{H}_2\text{BO}_3$ , and saturate with  $\text{H}_2\text{S}$ . Transfer to 40-ml conical centrifuge tube, centrifuge the  $\text{GeS}_2$  precipitate, and discard the supernate (Note 1).

Step 7. Dissolve the  $\text{GeS}_2$  in 1 ml of conc.  $\text{NH}_4\text{OH}$  and dilute to 15-20 ml with  $\text{H}_2\text{O}$ . Add 4 drops of Zr carrier, centrifuge and discard the precipitate. Make the supernate 3M with HCl, saturate with  $\text{H}_2\text{S}$ , centrifuge, and discard the supernate.

Step 8. Slurry the  $\text{GeS}_2$  with 4.5-5.5M HCl (Note 2) and transfer the solution to the special still. (The total volume of acid used should be about 15 ml.)

Step 9. Distill the  $\text{GeCl}_4$  on an oil bath at 120° into a 50-ml beaker containing 5 ml of 4.5-5.5M HCl saturated at room temperature with  $\text{H}_2\text{S}$  and placed in an ice bath (Note 3). 15-20 minutes are required before  $\text{GeCl}_4$  begins to distill over and then the distillation must be maintained for an additional 10-15 minutes to ensure completion. Very close to 100% yield is obtained in the distillation process.

Step 10. Transfer the distillate to another still and repeat the distillation.

Step 11. Saturate the receiver with  $\text{H}_2\text{S}$  and filter the precipitate onto a weighed No. 42 Whatman filter circle, 7/8" diameter, using a ground-off Hirsch funnel and a filter chimney. Wash the precipitate with anhydrous  $\text{CH}_3\text{OH}$  and dry in an oven at 110-120° for 10 minutes. Cool, weigh as  $\text{GeS}_2$ , and mount.

#### PROCEDURE 4 (Continued)

Notes: 1. A water-clear supernate is not ordinarily obtained upon centrifugation of the  $\text{GeS}_2$  unless the mixture is permitted to stand for several hours. Since the latter is not practicable, and since the losses are insignificant, do not hesitate to discard a slightly turbid supernate from a  $\text{GeS}_2$  precipitation.

2. The concentration of  $\text{HCl}$  must not exceed that of the constant boiling mixture or  $\text{GeCl}_4$  will escape during the distillation unless the delivery tube is below the surface of the receiving liquid. So long as the  $\text{HCl}$  concentration in the still is less than that required for the constant boiling mixture, only water and no  $\text{GeCl}_4$  is distilled. As soon as the composition of the still reaches that of the constant boiling mixture, all the  $\text{GeCl}_4$  comes over rapidly. At higher  $\text{HCl}$  concentrations the  $\text{GeCl}_4$  is immediately swept out with  $\text{HCl}$  gas.

3. The  $\text{H}_2\text{S}$  is present in the receiver to show (by the formation of white  $\text{GeS}_2$ ) when  $\text{GeCl}_4$  begins to distill.

#### PROCEDURE 5

Source "Preparation of Radioactive Germanium Radiochemically Pure"  
A. N. Baraboshkin  
Zhur. Neorg. Khim. 2, 2680-1 (1957)  
(translated from French Report CEA-Tr.-R-635 by Elyse R. Marinsky)

Radioactive germanium,<sup>1</sup> provided as the metal by industry, is not radiochemically pure. The quantity of residual activity is very great in certain specimens and makes up a large percent of the total radioactivity.<sup>2</sup> A part of the mixed radioactivities has more energetic radiation than that of germanium and likewise a greater half-life (11.4 days). With time the contribution of the residual activity increases.

For the utilization of radioactive germanium in physical or chemical processes, it is necessary to avoid erroneous conclusions by first purifying the samples removing the extra radioactivity.

The author has tested two methods of purification. The first consisted of a twice-repeated precipitation of germanium disulfide from a 6 N sulfuric acid solution and the ultimate dissolution of the precipitate on the filter paper with ammonia. The second method consists of the distillation of germanium tetrachloride from hydrochloric acid. One determines the effect-

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<sup>1</sup>The isotope  $^{71}\text{Ge}$  having a half-life of 11.4 days decays by orbital electron capture emitting characteristic x-rays.

<sup>2</sup>According to measurements of the radioactivity of the products by a counter of the Met-17 type, having a mica window thickness of 4.5 mg./cm<sup>2</sup>.

## PROCEDURE 5 (Continued)

iveness of purification and the degree of purity from aluminum absorption curves of the radiation.

The purification by the second method is more rapid and has been accomplished in the following manner: a sample of radioactive germanium metal was oxidized during its grinding in an agate mortar under a 1:1 mixture of concentrated hydrogen peroxide and 3 N potassium hydroxide. After 24 hours the contents of the mortar are placed in a quartz crucible and are evaporated to dryness. The residue is dissolved in hot water. The solution is neutralized with concentrated hydrochloric acid and transferred to a round bottom flask of a distillation apparatus. There one adds the same volume of hydrochloric acid ( $d = 1.10$ ) and proceeds with the distillation. Germanium disulfide is precipitated in the distillate with hydrogen sulfide. The precipitate is filtered, washed with 3 N sulfuric acid saturated with hydrogen sulfide and dissolved on the filter with concentrated ammonia. Hydrogen peroxide is added dropwise to the ammoniacal solution until disappearance of the yellow color (due to the decomposition of germanium disulfide). The solution is boiled until the decomposition of excess hydrogen peroxide and the elimination of free ammonia; the filtrate is transferred into a flask adjusting the volume to the calibration mark.

One sees that the absorption curves of the purified products develop according to the absorption law for monochromatic x-rays.

$$I = I_0 e^{-\mu d} \cdot e^{\mu \log I_0} = \log I_0 - 0.434 \mu d.$$

This fact shows that the two methods described provide in practice a radiochemically pure sample of the radioisotope  $^{71}\text{Ge}$ .

The principal part of residual activity is separated in the first stage of purification and remains, either in the filtrate after precipitation of the disulfide, or in the non-volatile residue from the distillation of the tetrachloride.

The author has not succeeded in identifying the elements of long half-life. However, he has specified that they are not coprecipitated with hydroxides of iron and zinc and the sulfates of calcium and barium.

## PROCEDURE 6

Source "Cyclotron Targets: Preparation and Radiochemical Separations. I. Arsenic and Germanium"

J. W. Irvine, Jr.

J. Phys. Chem. 46, 910 (1942)

An all-glass distilling apparatus utilizing a modified Claisen flask (250 ml.) has been found useful in several radiochemical separations. The coarse germanium powder from the bombarded target is placed in the flask and a standard solution of sodium arsenite added.

## PROCEDURE 6 (Continued)

The target material is treated with 25 ml. of 12 M hydrochloric acid, heated, and dissolved by the dropwise addition of 30 per cent hydrogen peroxide. This operation requires 10-20 ml. of hydrogen peroxide and takes about 5 min.

Germanium is removed as the volatile tetrachloride by distillation of the hydrochloric acid solution. Frequent additions of a few drops of hydrogen peroxide minimize reduction of  $As^{+5}$  to  $As^{+3}$  by the hydrochloric acid and contamination of the germanium by arsenic as arsenic trichloride. When solids precipitate from the solution in the flask, 10 ml. of 12 M hydrochloric acid is added and the distillation is repeated. Glass beads or pieces of tile will reduce bumping of the mixture during distillation.

Radiogermanium is recovered from the first two distillates by precipitation as the sulfide. Some radioarsenic will be found in these distillates. Although it usually amounts to no more than a few micrograms, its activity is large so it must be removed. Several milligrams of arsenic as sodium arsenite are added to the combined distillates and precipitated with ammonium hypophosphite with gentle heating. The metallic arsenic is filtered off, some more carrier added, and the precipitation repeated. Activity measurements on the precipitates indicate when the radioarsenic is completely removed. Two precipitations are usually adequate.

Germanium sulfide is then precipitated by adjusting the acidity to approximately 6 M and passing a rapid stream of hydrogen sulfide through the hot solution. The white germanium sulfide coagulates well and is easily filtered.

## PROCEDURE 7

Source "Chemical Separation of Fission Products"  
G. Wilkinson and W. E. Grummitt  
Nucleonics, Vol. 9, No. 3, pp. 54-55 (September, 1951)

### Fission-Product Procedures Germanium, Arsenic, and Selenium

The chemical procedures used were those of Noyes and Bray. Hold-back carriers and carriers for Ge, As, and Se in the various valency states were added to the U solution and the solution boiled under reflux with 40% HBr. The first distillate was collected, hold-back carriers were added, and a redistillation of the Ge, As and Se bromides was made. Selenium was precipitated from the second distillate by reduction with  $SO_2$  or  $NH_2OH \cdot HCl$ . The As was recovered as sulfide by  $H_2S$  precipitation from  $>5N$  HCl-HBr solutions or from HF solutions, Ge remaining in the filtrate in both cases. The Ge was recovered as sulfide after removal of HF by fuming with  $H_2SO_4$ .

Small amounts of I and Sn contamination were present in the Ge, As, and Se precipitates. These were dissolved in the minimum

## PROCEDURE 7 (Continued)

of  $\text{HNO}_3$ ,  $\text{I}^-$  carrier added, and  $\text{AgI}$  precipitated. The solutions were then made 6N in  $\text{HCl}$ ; Se was again reduced by  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and As and Ge were precipitated as sulfides from  $>2\text{N HCl}$ .

Inactive samples of Ge, As, and Se were obtained from samples containing over  $10^6$  disintegrations per minute of gross fission products, with chemical yields of 40-60%. Since no active species were found, the completeness of radiochemical exchange is not known.

## PROCEDURE 8

Source "Some Geochemical Determinations Using Radioactive and Stable Isotopes"

A. A. Smales, D. Mapper, J. Morgan, R. K. Webster and A. J. Wood  
A/Conf.15/P/282

The determination of copper, chromium, germanium, arsenic and antimony in iron meteorites by neutron activation

### Sample Treatment

Cubes of about 3-4 mm side were cut from the meteorite samples, care being taken to avoid inclusions as far as possible. The pieces were cleaned in dilute acid, washed and dried before being sealed into small silica ampoules. Two solutions, the first of 300  $\mu\text{g As/ml}$  and 10  $\mu\text{g Sb/ml}$ , and the second of 10 mg  $\text{Cr/ml}$ , 3 mg  $\text{Cu/ml}$  and 6 mg  $\text{Ge/ml}$ , were used as standards, quantities of about 0.1 ml being weighed and sealed into silica ampoules. Samples and standards were loaded into standard aluminium cans and irradiated in HEPO for two weeks.

After irradiation the samples were surface cleaned by rinsing with dilute acid, and then dissolved in a mixture of hydrochloric, nitric, hydrofluoric and perchloric acids, in the presence of 50 mg. arsenic, 40 mg. antimony, 20 mg. copper and germanium, and 10 mg. chromium as inactive carrier solutions. After taking to fumes of perchloric acid complete dissolution of the samples had taken place. The presence of hydrofluoric acid ensured that no losses of volatile germanium compounds occurred.

In the case of the troilite samples, a sintering technique with sodium peroxide was used, any insoluble residue being either dissolved in strong acid mixture, containing  $\text{HF}$ , or else being fused with potassium bisulphate.

After the addition of hydrochloric acid solution, 5 gm. of oxalic acid were added, and the sulphides of copper, arsenic and antimony completely precipitated with 2% thioacetamide solution. The germanium was precipitated from the filtrate, by the addition of 25 mls. of 5% tannic acid, and neutralization with ammonia.

The germanium precipitate was then treated with hydrochloric acid and hydrogen peroxide solution and the tetrachloride steam.

## PROCEDURE 8 (Continued)

distilled in the presence of arsenic, iron, cobalt and copper hold-back carriers. Germanium sulphide was finally precipitated from the distillate and then mounted on aluminium counting trays.

The copper, arsenic and antimony sulphides precipitate was purified as previously described and similarly prepared for counting, as cuprous thiocyanate, elemental arsenic and antimony trisulphide respectively.

The residual solution containing chromium was oxidized with nitric and perchloric acids, so that all the organic matter was destroyed and the chromium converted to chromate. The latter was then ether extracted as the peroxy-complex, purified from contaminating iron and cobalt activities, and finally prepared for counting as barium chromate.

All the counting was performed on automatic  $\beta$ -counting equipment, using thin-end-window Geiger-Muller tubes. Where advantageous, as for example for  $^{51}\text{Cr}$ , use was made of a  $\gamma$ -spectrometer with a 100-channel pulse height analyser. Radiochemical purity of the sample sources was checked in all cases, by decay measurements; in addition,  $\beta$ -energy absorption measurements and  $\gamma$ -spectrometer measurements were also used, where appropriate. Self-absorption corrections were applied in the  $\beta$ -counting of  $^{51}\text{Cr}$  and  $^{64}\text{Cu}$ .

The nuclides used were 12.8 hr.  $^{64}\text{Cu}$ ( $1.7 \times 10^6$ ), 27.8 day  $^{51}\text{Cr}$ ( $1.4 \times 10^5$ ), 12 hr.  $^{77}\text{Ge}$ ( $7.6 \times 10^3$ ), 26.5 hr.  $^{76}\text{As}$ ( $2 \times 10^6$ ) and 2.75 day  $^{122}\text{Sb}$ ( $1.1 \times 10^6$ ), the figures in brackets being the activity due to that nuclide in units of disintegrations/minute/ $\mu\text{g}$  of elements, after two weeks irradiation in the Harwell pile HEPO at a neutron flux of  $10^{12}\text{n/cm}^2/\text{sec}$ . In some cases alternative germanium nuclides were used, 82 min.  $^{75}\text{Ge}$ ( $8.2 \times 10^4$ ) or 11.4 day  $^{71}\text{Ge}$ ( $1.7 \times 10^5$ ).

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